



(11) **EP 2 418 017 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.02.2012 Bulletin 2012/07

(21) Application number: **11154278.3**

(22) Date of filing: **14.02.2011**

(51) Int Cl.:
B01J 37/04 ^(2006.01) **B01J 23/60** ^(2006.01)
B01J 23/652 ^(2006.01) **C07C 45/62** ^(2006.01)
C07C 45/73 ^(2006.01) **C07C 45/74** ^(2006.01)
C07C 49/203 ^(2006.01)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **15.08.2010 US 856653**

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(54) **Synthesis and use of a nano-crystalline zinc chromite catalyst, comprising nano-palladium**

(57) Several metal-supported catalyst compositions based on nano-crystalline zinc oxide were synthesized and characterized by X-ray powder diffraction (XRD), Carbon dioxide temperature programmed desorption (CO₂ TPD), and nitrogen adsorption at -196°C. The Pd-supported *nano*-ZnO mixed with different oxides such as Cr₂O₃, CrO₃, MgO, and γ -Al₂O₃ showed high catalytic activity in acetone condensation in gas-phase process under hydrogen flow. This reaction involves the base-

acid coupling of acetone to form mesityl oxide, followed by its hydrogenation to methyl isobutyl ketone (MIBK). The novel catalyst 1% wt. *n*-Pd/*n*-ZnCr₂O₄ was utilized during gas-phase reaction during production of MIBK. MIBK selectivity was 70-72% at 66-77% acetone conversion at 300-350° C. Diisobutyl ketone (DIBK) was the main by-product, with a total MIBK+DIBK selectivity up to 88%. The prepared catalysts showed stable activity and may be used repeatedly and for a longer period of time.

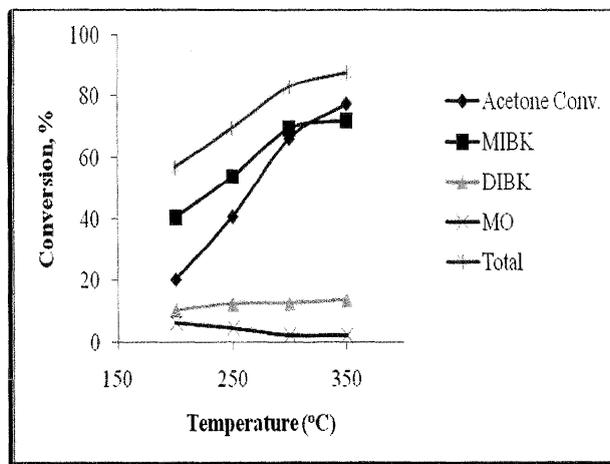


FIGURE 2

EP 2 418 017 A1

Description

FIELD OF TECHNOLOGY

5 **[0001]** This disclosure generally relates to synthesizing a novel nano-crystalline zinc chromite-supported nano-palladium catalyst and using the said novel catalyst to increase the production of methyl isobutyl ketone (MIBK).

BACKGROUND

10 **[0002]** Aldol condensation is a vital tool in organic synthesis to create carbon-carbon bond between two aldehyde or ketone molecules. The aldol product (β -hydroxyaldehyde or β -hydroxyketone) possesses hydroxyl and carbonyl functional groups, enabling its conversion via successive reactions to numerous industrially important products such as diols, α,β -unsaturated aldehydes, α,β -unsaturated ketones, saturated alcohols, allylic alcohols, aldehydes, and ketones. However, the aldol condensation is a reversible process, a feature that limits the utility of this reaction in term of conversion, especially when the starting material is a ketone because of unfavourable equilibrium. Acetone condensation is an example for the synthesis of highly important products such as methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK), phorone (PH), and α -isophorone (IPH) with low acetone conversion and low selectivity for the desired product.

15 **[0003]** MIBK is an important product derived from acetone. It is used as a solvent in paint and protective coating systems. MIBK is commercially produced using a three-step process. The main reaction pathways for the synthesis of MIBK from acetone are shown in Figure 1. The first step is the aldol addition of acetone to diacetone alcohol (DA, 4-hydroxy-4-methyl-2-pentanone). The second step is the aldol condensation of DA to mesityl oxide (MO, 4-methyl-3-penten-2-one). The final step is the selective hydrogenation of the carbon-carbon olefinic bond of MO to form MIBK. The most commonly observed side reactions are over-condensation and unselective hydrogenations.

20 **[0004]** Numerous catalysts are currently used in gas or liquid phase production of MIBK to obtain high yield with little success. The atmosphere, temperature and reaction phase play a vital role in the final yield of the MIBK.

25 **[0005]** The production processes are complicated and operational costs are high. The use of homogeneous liquid base and acid catalysts create a corrosive environment, require an additional neutralization process for their disposal, and generate a significant wastewater stream. Furthermore, the separation of DA and MO is mandatory for carrying out its successive step. Thus, there is a need for a better catalyst, which can be used in gas-phase production as well as in liquid phase production of MIBK. The MIBK production should provide a higher yield and, in turn, should become cost effective.

SUMMARY

35 **[0006]** The invention discloses a method of synthesizing a novel nano-crystalline zinc chromite-supported nano-palladium catalyst to increase the production of MIBK and other by products via one-step, gas-phase acetone self-condensation process.

40 **[0007]** In one embodiment, method of making a nano-crystalline zinc chromite-supported nano-palladium is described. Various combinations of platinum group metals and others were tested with zinc oxide. Several metals and different concentrations were tried to obtain a stable and effective catalyst.

[0008] In one embodiment, influence of the acid and basic properties of nano ZnO-based catalysts on the activity and selectivity for acetone condensation to MIBK was evaluated. In another embodiment, *nano*-ZnO was mixed with a metal oxide as an acid-base component and a platinum group metal as a hydrogenation component.

45 **[0009]** In another embodiment, characterizations of several properties of the novel nano-crystalline zinc chromite-supported nano-palladium catalyst were performed. This characterization was done to prove the purity and efficacy of the novel catalyst and to prove the current methods efficiency and effectiveness.

[0010] In another embodiment, optimization of a gas phase process of highly selective conversion of acetone to MIBK using nano-crystalline zinc chromite-supported nano-palladium catalyst was performed.

50 **[0011]** The novel catalyst composition, method of synthesizing the novel catalyst and method of utilizing the novel catalyst in chemical reactions disclosed herein may be implemented in any means for achieving various aspects. Other features will be apparent from the accompanying figures and from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

55 **[0012]** Example embodiments are illustrated by way of example and no limitation in the tables and in the accompanying figures, like references indicate similar elements and in which:

[0013] Figure 1 main reaction pathways in acetone condensation process.

[0014] Figure 2 shows acetone conversion and product selectivity's vs. reaction temperature on 1% wt. *n*-Pd/*n*-ZnCr₂O₄

(0.25 g catalyst, 15 5 ml/min H₂ flow, hydrogen/acetone = 2/1 mol, time-1hr).

[0015] Figure 3 shows Acetone conversion and product selectivity's vs. time on stream on 1% wt. *n*-Pd/*n*-ZnCr₂O₄ (0.25 g catalyst, 350°C, 15 ml/min H₂ flow, hydrogen/acetone = 2/1 mol).

5 [0016] Figure 4 shows results of Acetone conversion and product selectivity's vs. hydrogen flow rate on 1% wt. *n*-Pd/*n*-ZnCr₂O₄ (0.25 g catalyst, 350°C, time-1 hr).

[0017] Figure 5 shows the result of Acetone conversion and product selectivity's vs. time on stream on 1% wt. *n*-Pd/*n*-ZnO (0.25 g catalyst, 300°C, 15 ml/min H₂ flow, hydrogen/acetone = 2/1 mol).

[0018] Figure 6 shows XRD pattern of 1% wt. *n*-Pd/*n*-ZnCr₂O₄ catalyst and its match with database PDF No. 22-1107 of zinc chromite.

10 [0019] Other features of the present embodiments will be apparent from the accompanying figures, tables and from the detailed description that follows.

DETAILED DESCRIPTION

15 [0020] Several methods of synthesizing a novel *nano*-crystalline zinc chromite-supported *nano*-palladium catalyst and utilizing the novel catalyst to increase the production of MIBK and other by products are disclosed. Although the present embodiments have been described with reference to specific example embodiments, it will be evident that various modifications and changes may be made to these embodiments without departing from the broader spirit and scope of the various embodiments.

20

Preparation of Nano-Zinc Oxide:

25 [0021] Nano-zinc oxide (*n*-ZnO) was prepared with average crystallite size of 24.6 nm and BET specific surface area of 37.37 m²/g from zinc sulfate heptahydrate (BDH, 99.5%), sodium pyruvate (Sigma-Aldrich, ≥99%), sodium hydrogen carbonate (Fluka, ≥99.5%), hydroxylamine hydrochloride (Carlo Erba, 99%), and deionized water (18.2 MΩ.cm), obtained from a Milli-Q water purification system (Millipore). These chemicals were reacted with each other according to the weight ratio and number of moles shown in Table 1. Thermal decomposition of the zinc derivative of pyruvic acid oxime at 389°C was performed to eventually get *n*-ZnO.

30

Table 1. Weight ratio and mole ratio for the chemicals used to prepare *n*-ZnO.

Chemical Compound	Weight Ratio	Mole Ratio
Zinc sulfate heptahydrate	2.07	1
Sodium Pyruvate	1.58	2
Sodium hydrogen carbonate	1.22	2
Hydroxylamine hydrochloride	1.00	2

40

Preparation of *n*-ZnO mixture with other metal oxides:

45 [0022] The *n*-ZnO itself and its mixtures with different metal oxides such as γ-alumina, chromium(III) oxide, chromium (VI) oxide, magnesium oxide, and zeolites (ZSM-5 and USY) were used as supports. Metal oxides first were calcinated at 350° C for 5 hours under nitrogen flow. After calcination, they were mixed with nano zinc oxide in different ratios by mechanical stirring. These mixed metal oxides powder were then stirred with 0.02 M solution of metal salt at room temperature, followed by slow evaporation of the solvent in a rotary evaporator. The resulting powders were then reduced under hydrogen flow (50-60 ml/min) at 350° C for 5 hours, which eventually led to the formation of the required catalysts.

50 [0023] Surface area and pore diameter, of these catalysts were measured by N₂ adsorption at - 196°C using Autosorb-1-MP (Quantachrome, U.S.A) instrument. The basicity was estimated from CO₂ TPD obtained on TPD/R/O 1100 Thermo Electron instrument. X-ray powder diffraction (XRD) was recorded, on a Philips X' pert pro diffractometer operated at 40Kv by 40mA using CuK_α radiation in the 2 theta range from 2 to 100° in steps of 0.02° with a sampling time of 1s per step, for phase analysis and crystallite size measurement. The crystallite size was estimated using Scherer's equation.

55

[0024] The selectivity towards MIBK depends on the relative rates of above shown steps of acetone condensation. According to the chemical nature of different steps, aldol addition of acetone to DA is catalyzed by either basic or acidic sites, the aldol condensation of DA to MO is acid- or base-catalyzed, and the selective hydrogenation of MO to MIBK

requires metal sites.

[0025] In the present study, n-ZnO itself, and mixed with different metal oxides were chosen as acid-base components and platinum group metals for e.g. ruthenium, rhodium, palladium, osmium, iridium, and platinum etc., were used as hydrogenation component. The acetone self-condensation was studied in a fixed-bed flow reactor at 250-350° C, normal pressure, and H₂/acetone 2:1 mole ratio. The metal loading on catalysts was 1. wt%.

[0026] The textural properties named surface area (S_{BET}) pore diameter; basic site density, crystalline phases, and crystallite size of some catalysts used in this investigation are displayed in Table 2.

Table 2. N₂ adsorption, CO₂TPD and XRD characterization data.

Catalyst	S_{BET} , m ² /g	BJH average pore diameter, nm	CO ₂ ads., mmol/g	n_b ,* mmol/m ² 10 ⁻²	Crystalline Phase	Average crystallite size, nm
1%Pd/nanoZnO	33	---	0.281	0.85	ZnO (zincite)	29
1%Pd/nano ZnO/MgO	32	43.5	3.446	10.70	ZnO (zincite)	24
%Pd/ZnO/Cr ₂ O ₃ /Li ₂ O (1:10:1)	120	4.7	1.006	0.84	amorphous	---
1%Pd/nanoZnO/ γ -Al ₂ O ₃	61	38.9	0.669	1.09	ZnO (zincite)	21

*basic site density by TPD of CO₂.

[0027] From the results displayed in Table 1, it can be noticed that the n-ZnO-based catalysts have average crystallite size similar to that for n-ZnO itself, indicating that loading of Pd on and mixing this catalyst with other oxide in 1 wt% do not affect the crystallite size. Zincite phase was only observed for these catalysts and no Pd metal patterns were observed, indicating the presence of a very fine dispersion of Pd on the surface of this support. Such an observation was reported previously for Pd over mixed Zn-Cr oxide supports (Kozhevnikova et al.). The surface areas of the first catalysts in Table 1 are similar to that of n-ZnO itself. However, mixing the n-ZnO with 1 wt% γ -Al₂O₃ resulted in a surface area as twice as that of the nano ZnO and as those of the first two catalysts in Table 1. This increase in surface area can be attributed to the addition of the fine powder of γ -Al₂O₃. The mixed Zn-Cr-Li oxide has the highest surface area due to its amorphous nature. Such high surface area has been reported for mixed Zn-Cr³⁺oxide supports (Wadaani et al., Kozhevnikova et al.). The base site density (n_b) values for the first and third catalysts in Table 1 are similar and lower than the base densities of the other two catalysts containing γ -Al₂O₃ and MgO. The Pd/ZnO/MgO catalyst has the highest n_b due to the presence of MgO, which is well-known for its basicity.

Preparation of nano-crystalline zinc chromite-supported nano-palladium:

[0028] The synthesized n-ZnO was mixed and pulverized with the commercially available chromic oxide (CrO₃, Fluka) in a 1:1 mole ratio and with an appropriate amount of palladium acetate [Pd(OOCCH₃)₂, Aldrich], which yields 1% wt loading of palladium nanoparticles after the reduction process under hydrogen atmosphere (99,999%, Abdullah Hashim, Ltd.). Table 3 shows an example of the weight ratio and mole ratio used for mixing the n-ZnO, CrO₃ and Pd(OOCCH₃)₂. Anhydrous, thiophene-free benzene (25 ml, Fisher Scientific) was added to this solid mixture to dissolve Pd(OOCCH₃)₂. The resultant suspension was mechanically stirred. Benzene was evaporated under vacuum at ambient temperature, over a period of 24 hours, by using a rotary evaporator. After drying, benzene was added and subsequently was evaporated twice more to ensure the homogeneous distribution of the palladium nanoparticle on the support of the final catalyst. After the third drying process, the resultant solid was ground and then was heated under a hydrogen flow of 50 ml/min at 350°C for five hours in a digital, programmable, tubular muffle furnace. The temperature was ramped from the ambient to the target at a rate of 10°C/min. Cooling to the ambient was also performed at the same rate of heating. The obtained catalyst [1% wt. n-Pd/n-ZnCr₂O₄] after this reduction process was kept under hydrogen in desiccators until its use. The weight in gram could be n-ZnO between the range of 0.5 g to 2.0 g, CrO₃ between the range of 0.5 to 2.0 g and Pd(OOCCH₃) between the range of 0.01- 1.0g. These are suggested range and limitations.

Table 3. Weight quantities and number moles of *n*-ZnO, CrO₃, and Pd(OOCCH₃)₂

Chemical Compound	Weight Ratio	Mole Ratio
<i>n</i> -ZnO	21.10	54.33
CrO ₃	25.92	54.33
Pd(OOCCH ₃) ₂	1.00	1.00

[0029] Characterization of this catalyst by X-ray powder diffraction (XRD) technique showed a pattern of broad peaks, matched with that of zinc chromite [ZnCr₂O₄](Figure 6). The broadness of the peaks implies the formation of nanocrystalline phase, which was confirmed by the average crystallite size of 18.65 nm, estimated by applying the Scherrer's equation to four peaks, as it displayed in Table 4.

Table 4. Calculation of the average crystallite size of the ZnCr₂O₄ phase of the 1% wt. *n*-Pd/*n*-ZnCr₂O₄ catalyst, based on Scherrer's equation.

2-Theta	Crystallite Size (nm)
30.2	16.46
35.7	16.70
43.2	21.37
75.25	20.07

Average crystallite size = (16.46 + 16.70 + 21.37 + 20.07)/4 = 18.65 nm

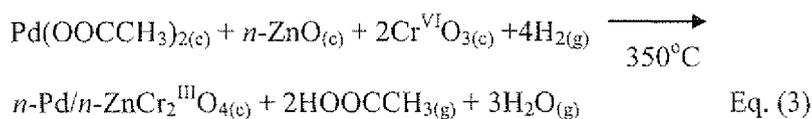
[0030] Furthermore, observation of the chromite phase had the implication of reducing the hexavalent chromium [Cr(VI)] to the trivalent chromium [Cr(III)] under the reduction conditions, applied for the catalyst preparation, as illustrated in the following chemical equation:



[0031] This XRD spectrum (Figure 6), in addition, did not display any characteristic patterns due to palladium metal. Such observation implies the formation of highly dispersed palladium metal nanoparticles. The reduction of the palladium bivalent to the zero-valent metallic palladium nanoparticles by hydrogen is illustrated in equation 2 below:



[0032] The formation of nanocrystalline zinc chromite-supported nano-palladium catalyst can be given by the summation of equation 1 and equation 2, as represented in equation 3:



Catalytic gas-phase acetone self-condensation:

[0033] The acetone self-condensation was performed in a temperature range of 250-350°C, under atmospheric pressure, in a tubular glass fixed-bed microreactor (ID 0.9 cm), under H₂ or N₂ atmosphere at a H₂/acetone mole ratio of 2. The reactor was placed in a vertical tubular furnace. A catalyst sample (~0.25 g) was loaded into the reactor between two layers of Pyrex glass wool and pieces of ceramics. A K-type thermocouple was placed in the center of the catalyst to monitor the reaction temperature. Acetone was introduced to the reactor by a Hitachi HPLC pump (Model L-2100/2130), connected to a heated tube (65-70°C) for its delivery as a vapor mixed with H₂ or N₂ before entering the reaction zone at the top of the catalyst bed. The acetone was pumped at a continuous flow. The reaction liquid products were trapped at -40°C, were collected every one hour, and were analyzed off-line by using a Varian CP-3800 gas chromatograph, equipped with a flame ionization detector (FID) and a 50 m x 0.32 mm x 1.2 mm CP-Wax 58 CB column. The gaseous downstream flow was analyzed online by a refinery gas analyzer (RGA) Varian CP-3800 GC, equipped with an FID and a thermal conductivity detector (TCD). The products were identified by GC, using authentic samples.

[0034] MIBK was the major reaction product and a significant amount of diisobutyl Ketone (DIBK) was also formed. Maximum selectivity for MIBK was observed at 300-350°C (Table 5). By-products included isopropyl alcohol (IPA) and other acetone condensation compounds such as mesitylene (M), DA, IPH, and PH. In the gaseous phase, a small amount of propene and propane were also detected.

Table 5. Gas-phase condensation of acetone on nano ZnO-based catalysts.

Catalyst	Temp., °C	Conv., %	Selectivity, %						
			MIBK	DIBK	MO	M	IPA	DA	Others
Nano ZnO	300	20.9	2.0	trace	55.8	2.6	9.5	1.4	28.7
Nano ZnO*	300	7.1	5.8	trace	73.7	1.3	trace	trace	19.2
1%Pd/nano ZnO	300	53.9	56.2	22.4	2.3	3.2	7.6	3.5	4.9
1%Pd/nano ZnO*	300	10.3	3.5	1.4	87.1	1.2	3.5	trace	3.3
1%Pd/ZnO/Cr ₂ O ₃ (1:10)	300	60.2	42.4	28.7	1.9	5.6	2.5	11.1	7.8
1%Pd/ZnO/Cr ₂ O ₃ /MgO (1:10:1)	300	74.7	41.8	26.9	1.1	5.7	2.2	10.4	11.9
1%Pd/nano ZnO/CrO ₃ (1:1)	300	66.1	69.4	12.4	2.1	4.6	3.9	3.9	4.0
1%Pd/nano ZnO/CrO ₃ (1:1)	350	77.3	72.1	13.5	2.2	2.7	4.4	2.5	2.6
1%NiRc/ZSM-5/Al ₂ O ₃	300	23.8	44.2	12.3	8.6	0.7	3.9	4.6	25.7
1%Pt/USY	300	9.7	60.9	trace	4.4	7.3	trace	trace	27.4

Reaction conditions: 0.25 g catalyst, 15 ml/min H₂ flow, hydrogen/acetone = 2/1 mol, time on stream-1 hr.

*N₂ was used instead of H₂ (15 ml/min).

[0035] Pd was found to be the most effective among metals used for the hydrogenation function of catalysts. The 1% wt. *n*-Pd/*n*-ZnCr₂O₄ gave the most active and selective catalyst for direct synthesis of MIBK from acetone. The highest MIBK selectivity of 72.1% was obtained at 77.3 wt% acetone conversion at 350°C. The total MIBK and DIBK selectivity of 85.6% was obtained at these conditions (Table 5, Fig.2).

[0036] *n*-Pd/*n*-ZnO without any other component was also selective catalyst for the synthesis of MIBK (selectivity 56.2%). When *n*-ZnCr₂O₄ was used in the N₂ atmosphere in the absence of hydrogen, MO was the major product. The same results were achieved when reaction was carried out on *n*-ZnCr₂O₄ under H₂ atmosphere in the absence of Pd. These results showed that the *n*-ZnCr₂O₄ itself acted mainly as an acidic-basic catalyst. The *n*-Pd/nano-ZnO and 1% wt. *n*-Pd/*n*-ZnCr₂O₄ catalysts exhibited very good stability (Fig 3-5). No catalyst deactivation was observed during 50 hours of continuous operation. With increasing reaction temperature, acetone conversion increased from 23.6% at 200°C to 77.3% at 350°C. Under these conditions, MIBK selectivity also increased from 40.6.0% to 72.1%.

[0037] In addition, the specification and drawings are to be regarded in an illustrative rather than as in a restrictive sense.

Claims

1. A catalyst, comprising;

a platinum group metal;
a metal oxide; and
a *nano*-zinc oxide.

- 5 **2.** The catalyst as in claim 1, wherein the platinum group of metal is at least one of ruthenium, rhodium, palladium, osmium, iridium, and platinum.
- 3.** The catalyst as in claim 2, wherein the platinum group of metal is palladium acetate.
- 10 **4.** The catalyst as in claim 3, wherein palladium acetate is reduced to a *nano*-palladium.
- 5.** The catalyst as in claim 1, wherein the metal oxide is a chromic oxide.
- 6.** The catalyst as in claim 1, further comprising of a formula of $n\text{-Pd}/n\text{-ZnCr}_2\text{O}_4$.
- 15 **7.** A method of making the catalyst, comprising:
- reacting zinc sulfate heptahydrate, sodium pyruvate, sodium hydrogen carbonate and hydroxylamine hydrochloride to produce a *nano*-ZnO;
20 calcinating the metal oxide under nitrogen flow to produce a metal oxide powder; and
 mixing the *nano*-ZnO and the metal oxide powder in a ratio to form a *nano*-ZnO-metal oxide mix.
- 8.** The method of claim 7, further comprising:
- 25 dissolving a platinum group metal salt in a thiophene-free benzene by mechanical stirring;
 mixing the *nano*-ZnO-metal oxide mix with the platinum group metal salt dissolved in thiophene-free benzene to form a pre-catalyst;
 evaporating the benzene under vacuum at ambient temperature using rotary evaporator to dry the pre-catalyst;
 reducing the dried pre-catalyst under a steady flow of hydrogen at 350° C in a tubular muffle furnace;
30 heating and cooling the pre-catalyst to obtain a catalyst by a reduction process; and
 storing the catalyst under at least one of nitrogen and argon in desiccators until further use.
- 9.** The method of claim 7, wherein the metal oxide is a chromic oxide.
- 35 **10.** The method of claim 8, wherein the salt of platinum group of metal is at least one of ruthenium, rhodium, palladium, osmium, iridium, and platinum.
- 11.** The method as in claim 9, wherein the salt of platinum group of metal is palladium acetate.
- 40 **12.** The method of claim 11, wherein palladium acetate is reduced to *nano*-palladium metal.
- 13.** The method of claim 12, wherein the catalyst formed has a formula of 1% wt. $n\text{-Pd}/n\text{-ZnCr}_2\text{O}_4$.
- 14.** A process, comprising;
- 45 synthesizing a *nano*-ZnO;
 mixing a metal oxide to *nano*-ZnO;
 synthesizing a nano-palladium/nano-Zn-metal oxide catalyst; and
 producing at least one of a MIBK, DIBK, MO, M and IPA using the nano-palladium/nano-Zn-metal oxide catalyst
50 from acetone self-condensation.
- 15.** The process of claim 14, wherein the metal oxide is chromic oxide (CrO_3).
- 16.** The process of claim 14, further comprising:
- 55 producing *nano*-ZnO by reacting zinc sulfate heptahydrate, sodium pyruvate, sodium hydrogen carbonate and hydroxylamine hydrochloride;
 flowing steady stream of nitrogen over the metal oxide during the calcinations of metal oxide to produce a metal

oxide powder; and
synthesizing a *nano-ZnO-metal-oxide* mix by mixing a 1 :1 mole ratio of the metal oxide powder and *nano-ZnO*.

5
17. The process of claim 14, further comprising:

mechanically stirring the platinum group of metal salt in thiophene-free benzene to make a metal-salt solution;
mixing the *nano-ZnO-metal* oxide mix with the platinum group metal salt dissolved in thiophene-free benzene
to form a pre-catalyst;
performing rotary evaporation of the benzene under vacuum at ambient temperature to dry the pre-catalyst;
10 maintaining a steady flow of hydrogen in a known rate to reduced the pre-catalyst at 350° C; ,
cooling and heating the pre-catalyst to obtain a catalyst by a reduction process; and
storing the catalyst under under at least one of nitrogen and argon in desiccators until further use.

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18. The process of claim 17, further comprising:

placing a catalyst between two layers of pyrex glass wool and pieces of ceramic; and
loading the catalyst into a reactor.

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19. The process of claim18, further comprising:

vaporizing acetone at a temperature between 65-70 °C;
mixing the vaporized acetone at least one of H₂ and N₂ gas as a mix;
pumping the mix in a continuous flow into the reactor under atmospheric pressure; and
25 maintaining the temperature of the reactor between 250-350 °C.

30
20. The process of claim 19, further comprising:

collecting a liquid product that was formed and analyzing the liquid product every hour
using a gas chromatography equipment; and
35 analyzing a gas product using a gas analyzer to identify and quantify the gas product.

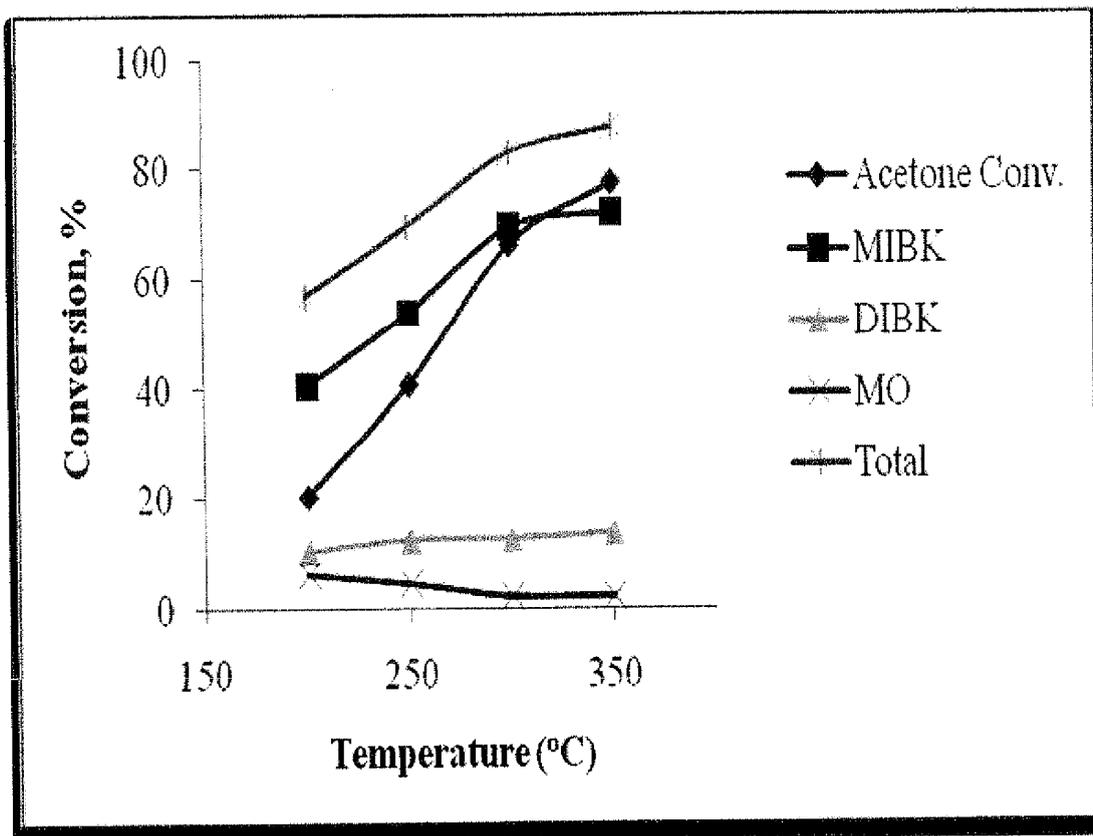


FIGURE 2

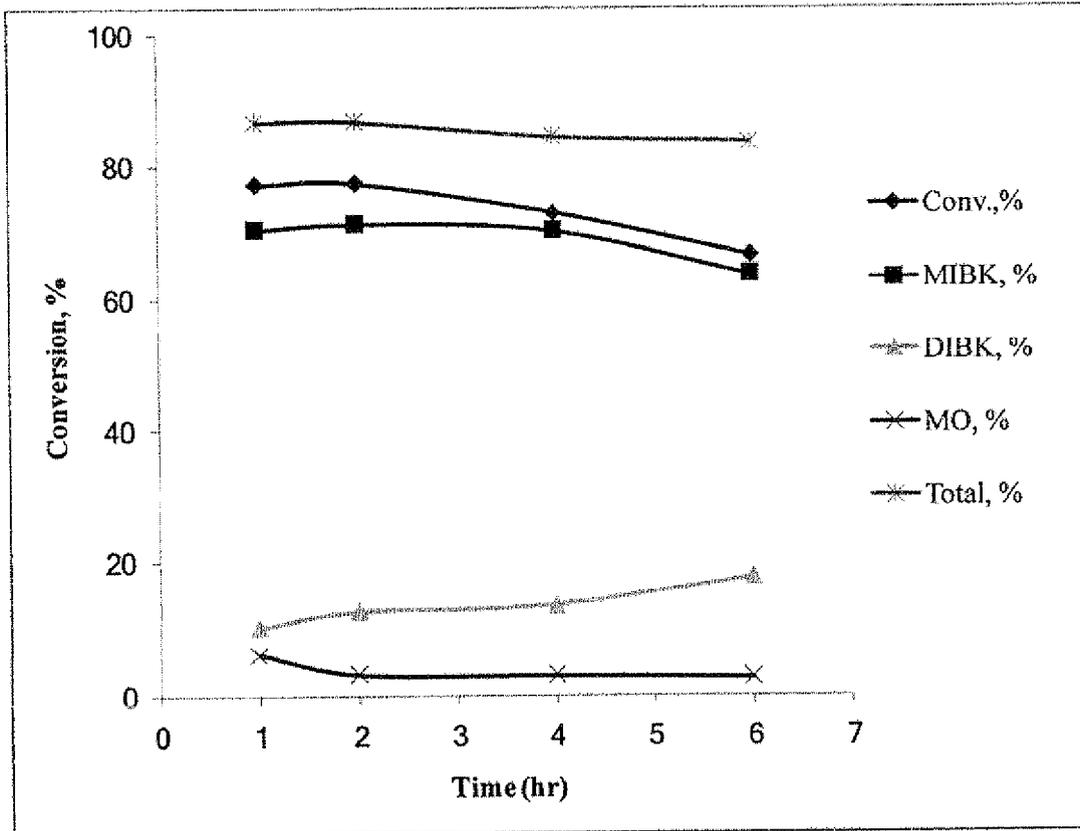


FIGURE 3

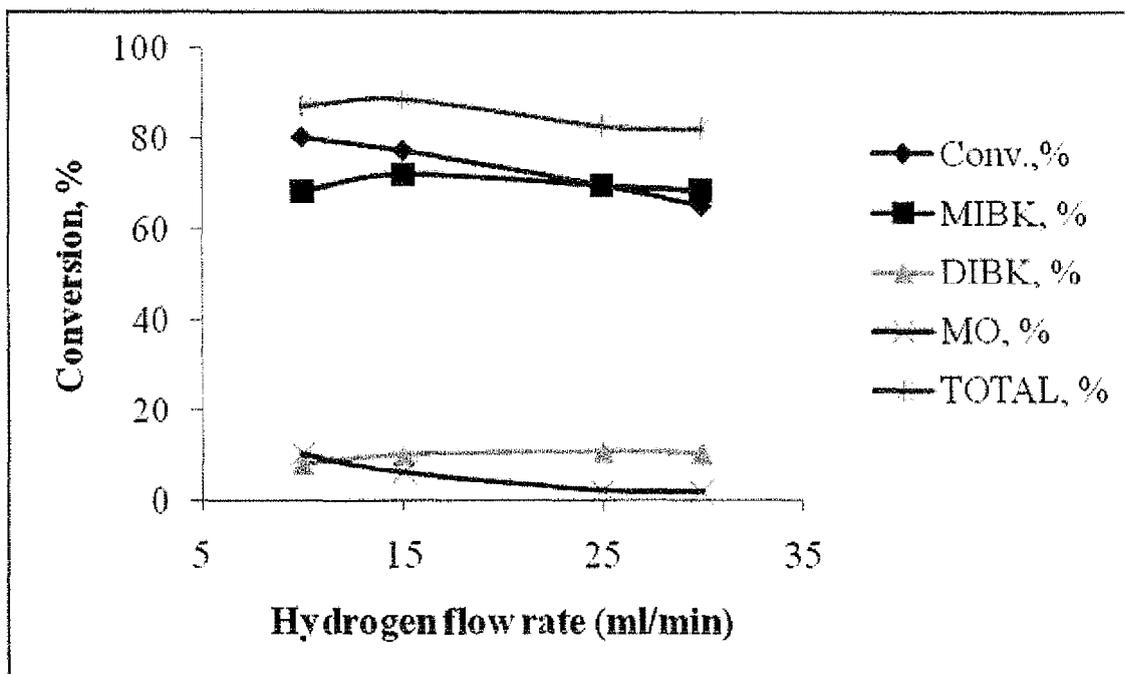


FIGURE 4

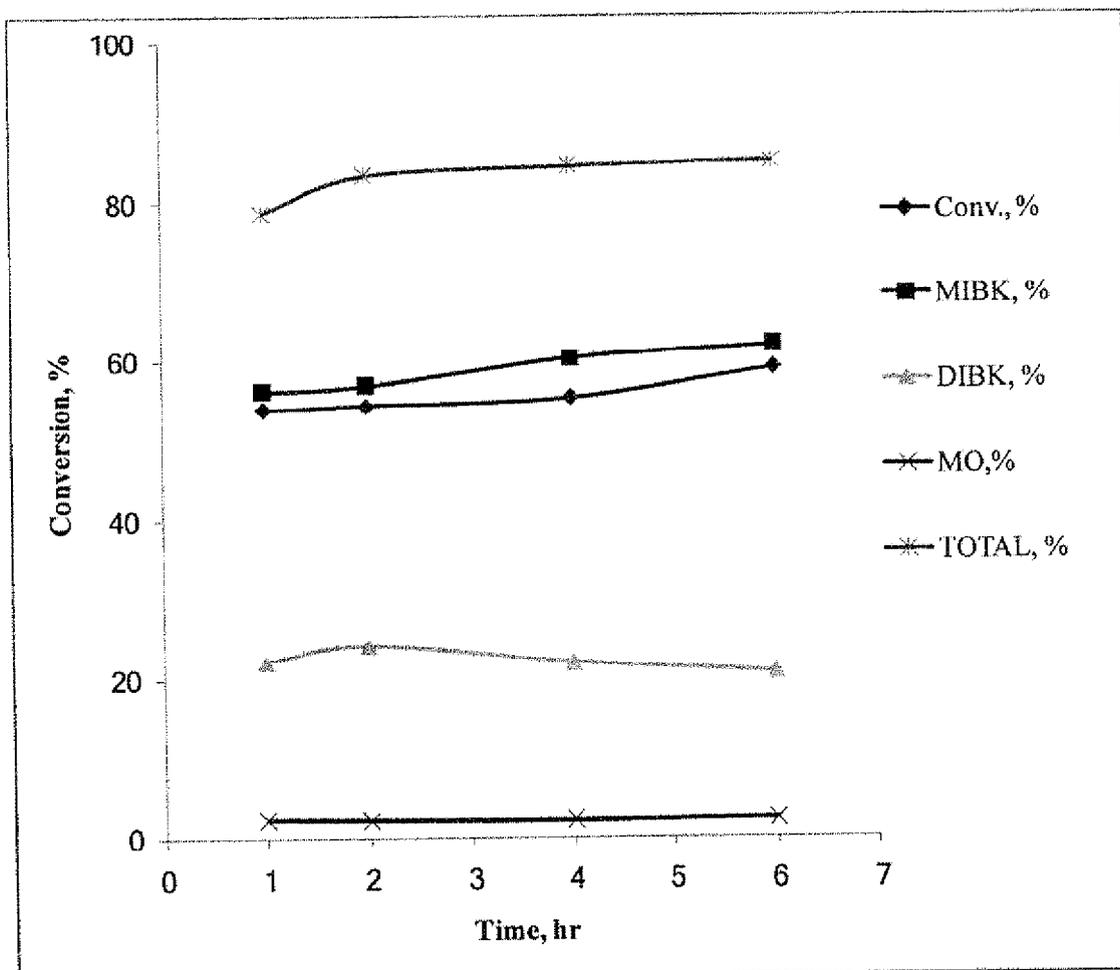


FIGURE 5

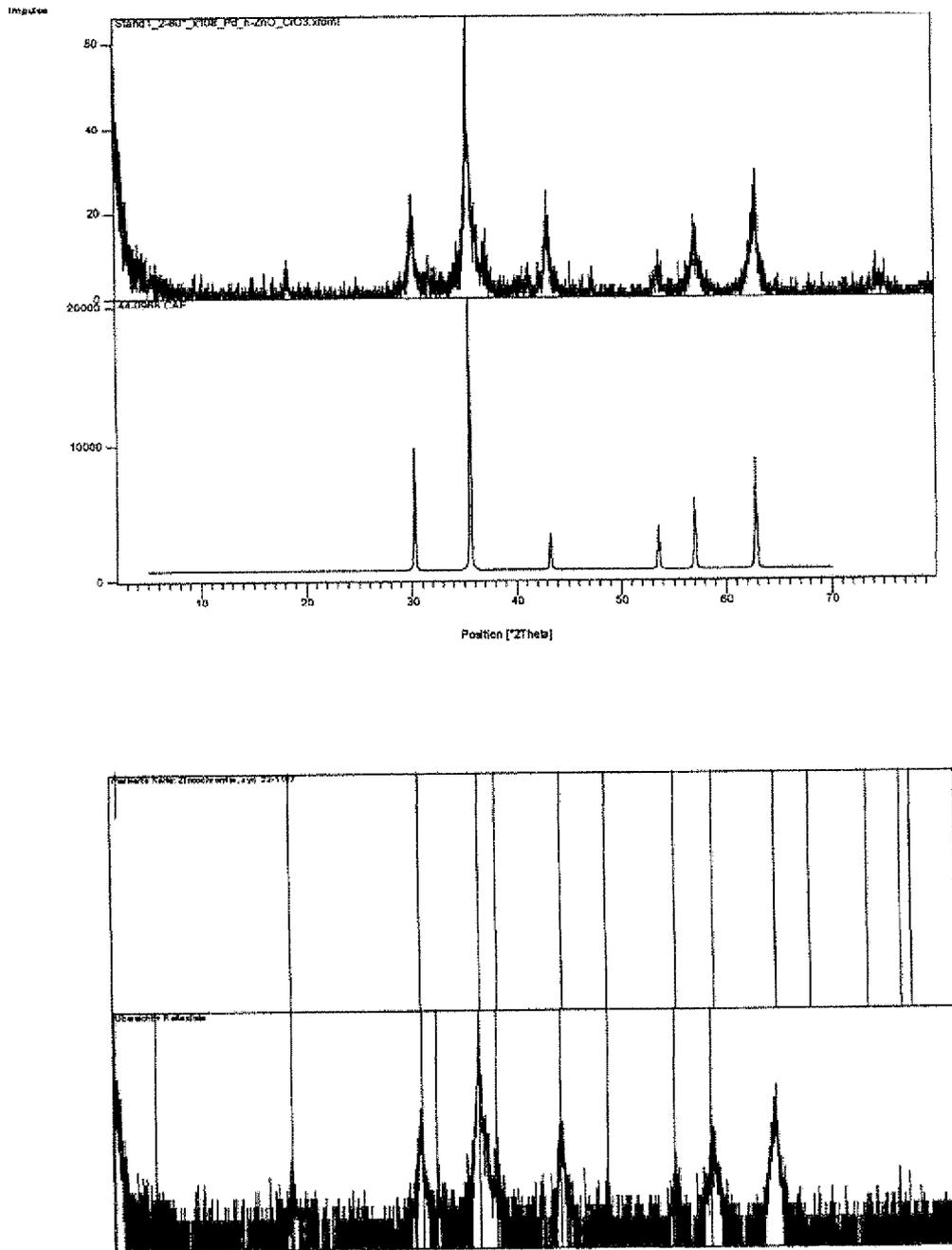


FIGURE 6



EUROPEAN SEARCH REPORT

Application Number
EP 11 15 4278

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 312 413 A2 (MITSUBISHI GAS CHEMICAL CO [JP]) 21 May 2003 (2003-05-21) * claims 1-5, 8, 9 * * paragraph [0014] * * paragraph [0021] - paragraph [0026] * * paragraph [0032] - paragraph [0033] * * paragraph [0037] * * paragraph [0050] - paragraph [0056] * * tables 1-4 * * paragraph [0072] - paragraph [0074] * * paragraph [0076] - paragraph [0077] * * tables 7, 8 * * paragraph [0086] - paragraph [0088] * * paragraph [0091] - paragraph [0092] * * tables 11, 12 *	1-6	INV. B01J37/04 B01J23/60 B01J23/652 C07C45/62 C07C45/73 C07C45/74 C07C49/203
X	WO 88/00189 A1 (BRACCO IND CHIMICA SPA [IT]) 14 January 1988 (1988-01-14) * claims 1-10 * * page 2, line 24 - line 30 * * page 3, line 28 - page 4, line 3 * * example 1 *	1,2,5,6	TECHNICAL FIELDS SEARCHED (IPC)
X	US 2002/143180 A1 (POTHARAJU SEETHARAMANJANEYA SA [IN] ET AL) 3 October 2002 (2002-10-03) * paragraph [0002] * * paragraph [0004] * * paragraph [0019] * * paragraph [0021] * * paragraph [0028] * * example 1 *	1,2,5,6	B01J C07C
----- -/--			
The present search report has been drawn up for all claims			
2	Place of search Munich	Date of completion of the search 24 October 2011	Examiner Kyriopoulos, Aliko
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
EP 11 15 4278

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 2003 160302 A (MITSUBISHI GAS CHEMICAL CO) 3 June 2003 (2003-06-03) * claim 1 * * paragraph [0007] - paragraph [0012] * * paragraph [0016] * * paragraph [0018] * * paragraph [0021] - paragraph [0023] * -----	1-6	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 24 October 2011	Examiner Kyriopoulos, Alik
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 15 4278

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-10-2011

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1312413	A2	21-05-2003	US 2003157019 A1	21-08-2003
WO 8800189	A1	14-01-1988	AU 7644587 A	29-01-1988
			IT 1196480 B	16-11-1988
US 2002143180	A1	03-10-2002	NONE	
JP 2003160302	A	03-06-2003	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82