CATALYTIC OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

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Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

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Filed: Sept. 30, 1996

FOREIGN PATENT DOCUMENTS

2004219 5/1990 Canada.
9006297 6/1990 WIPO
WIPO 90/06282 6/1990

OTHER PUBLICATIONS


Abstract

A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof comprising reacting said hydrocarbons and molecular oxygen in the presence of a platinum catalyst. The catalyst consists essentially of platinum modified with Sn or Cu and supported on a ceramic monolith.

16 Claims, 6 Drawing Sheets
### U.S. PATENT DOCUMENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
</tr>
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<tbody>
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### OTHER PUBLICATIONS


FIG. 9
**FIG. 10**

Graph showing the conversion of n-butane (% n-C4H10) vs. n-C4H10/O2 ratio for different catalysts:
- Pt-Cu
- Pt-Sn
- Pt

**FIG. 11**

Graph showing the conversion of i-butane (% i-C4H10) vs. i-C4H10/O2 ratio for different catalysts:
- Pt-Cu
- Pt-Sn
- Pt
1. CATALYTIC OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

This is a division of application Ser. No. 08/589,387 filed Jan. 22, 1996 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to oxidation/dehydrogenation catalysts and a process for the dehydrogenation of dehydrogenable hydrocarbons in the presence of an oxygen-containing gas. This invention was made with government support under grant number CTS 9311.295 awarded by the National Science Foundation. The government has certain rights in the invention.

The dehydrogenation of hydrocarbons is an important commercial process. This is because of the great demand for dehydrogenated hydrocarbons as feedstocks for industrial processes. For example, dehydrogenated hydrocarbons are utilized in the manufacture of various products such as detergents, high octave gasoline, and pharmaceutical products among others. Plastics and synthetic rubbers are other products which may be produced through use of dehydrogenated hydrocarbons. One example of a specific dehydrogenation process is dehydrogenating isobutane to produce isobutene which may be etherified to produce gasoline octane improvers, polymerized to provide adhesive tackifying agents, viscosity-index additives and plastic antioxidants.

2. Related Art

Various reticulated ceramic structures are described in the art: U.S. Pat. No. 4,251,239 discloses a filter of porous ceramic having increased surface area; U.S. Pat. No. 4,508,595 discloses reticulated ceramic foams with a surface having a ceramic sintered coating closing off the cells; U.S. Pat. No. 3,900,646 discloses ceramic foam with nickel coating followed by platinum deposited in a vapor process; U.S. Pat. No. 3,957,658 discloses nickel or palladium coated on a negative image ceramic metal/ceramic or metal foam; U.S. Pat. No. 3,898,758 discloses ceramic foam with nickel, cobalt or copper deposited in two layers with the second layer reinforced with aluminum, magnesium or zinc; U.S. Pat. Nos. 4,810,685 and 4,863,712 disclose negative image reticulated foam coated with active material, such as, cobalt, nickel or molybdenum coating; U.S. Pat. No. 4,308,233 discloses a reticulated ceramic foam having an activated alumina coating and a noble metal coating useful as an exhaust gas catalyst; U.S. Pat. No. 4,253,302 discloses a foamed ceramic containing platinum/rhodium catalyst for exhaust gas catalyst, and U.S. Pat. No. 4,088,607 discloses a ceramic foam having an active aluminum oxide layer coated by a noble metal containing composition such as zinc oxide, platinum and palladium.

The supports employed in the present invention are generally of the type disclosed in U.S. Pat. No. 4,810,685 using the appropriate material for the matrix and are generally referred to in the art and herein as ‘monoliths’.

The monoliths with various catalytic materials deposited thereon have also been employed for the production of synthesis gas (PCT WO 90/06279) and nitric acid (U.S. Pat. No. 5,217,939)

U.S. Pat. No. 4,940,826 (Freid, et al) discloses the oxidative dehydrogenation of gaseous paraffinic hydrocarbons having at least two carbon atoms or a mixture thereof by contacting the hydrocarbon with molecular oxygen containing gas over a supported platinum catalyst where the support is alumina such as gamma alumina spheres and monoliths such as cordierite or multile. The desired products are the corresponding olefins.

Various modifiers are disclosed for the monolith/noble metal. Canadian patent 2,004,219 lists Group IV elements as coating materials for monoliths and U.S. Pat. No. 4,927,857 discloses a platinum monolith partial oxidation catalyst supplemented with copper used in conjunction with a steam reforming process. Neither of these references suggests the use of modified platinum monolith catalyst in oxidative dehydrogenations.

SUMMARY OF THE INVENTION

Briefly, the present invention is a process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof comprising reacting said hydrocarbons and molecular oxygen in the presence of a platinum catalyst modified with Sn or Cu, preferably in the substantial absence of Pd and Rh on a monolith support. The catalysts consist essentially of platinum modified with Sn or Cu on a ceramic monolith support, preferably alumina or zirconia monolith support.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows ethane conversion as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 2 shows ethylene selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 3 shows ethylene yield as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 4 shows CO selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 5 shows CO₂ selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 6 shows H₂ selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 7 shows H₂O selectivity as a function of the ethane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

FIG. 8 plots the conversion of ethane and ethylene selectivity as a function of the ratio of Sn:Pt.

FIG. 9 illustrates the effect of feed preheating on ethane conversion, ethylene selectivity and ethylene yield.

FIG. 10 shows n-butane conversion as a function of the butane:oxygen ratio for Sn and Cu modified Pt monolith.

FIG. 11 shows i-butane conversion as a function of the i-butane:oxygen ratio for Sn and Cu modified Pt monolith catalyst compared to Pt alone.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The composition of the ceramic support can be any oxide or combination of oxides that is stable at the high temperatures of operation, near 1000° C. The support material should have a low thermal expansion coefficient. The com-
Components of the oxide support should not phase separate at high temperatures since this may lead to loss of integrity. Components of the oxide support should not become volatile at the high reaction temperatures. Suitable oxide supports include the oxides of Al (α-Al₂O₃), Zr, Ca, Mg, Hf, and Ti. Combinations of these can be produced to tailor the heat expansion coefficient to match the expansion coefficient of the reactor housing.

The structure and composition of the support material is of great importance. The support structure affects the flow patterns through the catalyst which in turn affects the transport to and from the catalyst surface and thus the effectiveness of the catalyst. The support structure should be identical to those described but experiments were less extensive for poor catalysts (Pt/Mg, Pt/Ce, Pt/Ni, Pt/La, Pt/Co). The addition of the other metals lowered both conversion and olefin selectivity in the order of Sn<Co<Pt alone>Ag>Mg>Ce>Ni>La>Co as demonstrated with ethene. With lower C₂H₄ selectivity, syngas (CO+H₂) formation became predominant. Pt/Al could not be ignited with C₂H₄+O₂. NH₃ and O₂ were used for light-off of the Pt/Al catalyst, however, the catalyst extinguished quickly when C₂H₆ was introduced in spite of the presence of NH₃.

The results on the catalysts containing the various metals were summarized in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atomic ratio (Metal:Pt)</th>
<th>Reaction temp °C</th>
<th>Conv. of C₂H₄ %</th>
<th>S₉-C₃H₄ %</th>
<th>S₂C₈ %</th>
<th>Y₂H₂C₃H₄ %</th>
<th>Max. Y₂H₂C₃H₄ (in C₂H₆O₂)</th>
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<tbody>
<tr>
<td>Pt</td>
<td>0</td>
<td>920</td>
<td>69.7</td>
<td>64.9</td>
<td>26.9</td>
<td>45.3</td>
<td>52.7 (1.5)</td>
</tr>
<tr>
<td>Pt/Sn</td>
<td>1</td>
<td>912</td>
<td>71.5</td>
<td>68.2</td>
<td>24.1</td>
<td>48.8</td>
<td>55.3 (1.5)</td>
</tr>
<tr>
<td>Pt/Ce</td>
<td>3</td>
<td>905</td>
<td>72.8</td>
<td>68.0</td>
<td>24.4</td>
<td>49.5</td>
<td>55.4 (1.5)</td>
</tr>
<tr>
<td>Pt/Ni</td>
<td>3</td>
<td>920</td>
<td>75.7</td>
<td>69.0</td>
<td>21.9</td>
<td>52.3</td>
<td>57.4 (1.7)</td>
</tr>
<tr>
<td>Pt/Cu</td>
<td>7</td>
<td>928</td>
<td>74.4</td>
<td>68.1</td>
<td>23.6</td>
<td>50.7</td>
<td>55.0 (1.7)</td>
</tr>
<tr>
<td>Pt/Cu</td>
<td>3</td>
<td>928</td>
<td>74.4</td>
<td>68.1</td>
<td>23.6</td>
<td>50.7</td>
<td>55.0 (1.7)</td>
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<tr>
<td>Pt/Ag</td>
<td>3</td>
<td>943</td>
<td>65.1</td>
<td>60.6</td>
<td>33.6</td>
<td>39.5</td>
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<td>Pt/Mg</td>
<td>3</td>
<td>965</td>
<td>60.2</td>
<td>40.7</td>
<td>47.7</td>
<td>20.9</td>
<td>31.2 (1.7)</td>
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<tr>
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<td>905</td>
<td>56.0</td>
<td>41.7</td>
<td>56.0</td>
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<td>24.8 (1.7)</td>
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<tr>
<td>Pt/Al</td>
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<td>905</td>
<td>58.7</td>
<td>46.3</td>
<td>50.4</td>
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<td>29.3 (1.7)</td>
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<tr>
<td>Pt/Co</td>
<td>1</td>
<td>873</td>
<td>50.8</td>
<td>29.8</td>
<td>71.4</td>
<td>13.1</td>
<td>15.3 (1.7)</td>
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</table>

Note: All conversions, selectivities, and temperatures at C₂H₆O₂ = 1.9 and 5 slpm without preheater. Pt loadings of all catalysts are 2 wt%.

The paraffins which are suitable for the present process are generally those that can be vaporized at temperatures in the range of 25 to 400°C at pressures of 0.1 to 5 atm. These are generally C₃ to C₂₀ carbon atom alkanes either alone or in mixtures, preferably having two to eight carbon atoms. Suitable alkanes include ethane, propane, n-butane isobutane, n-pentane, isopentane, hexane, isoalkanes, n-heptane, isohexane, octane and isooctanes. Since a preferred embodiment includes a preheating of the feed to the reaction zone, the necessity to heat an alkane feed above ambient temperature to obtain a vaporous feed is not a negative consideration.

The feed may include both linear and branched alkanes. It has been observed in a fuel rich regime for the oxidative dehydrogenation of n-butane that the oxygen is completely consumed, whereas for the isobutane oxidations it is not. This oxygen breakthrough suggests a rate limiting step for isobutane. It is a proposed theory that the rates of these reactions, should be related to the strengths of C—H bonds that must be broken. Thus, it may be desirable to preheat these feeds which are determined to have relatively strong C—H bonds to increase the rate of the initiation step. The feeds may be preheated to temperatures in the range of 0 to 500°C, preferably 25 to 400°C.

The present invention discloses the catalytic oxidative dehydrogenation of hydrocarbons. Mixtures of hydrocarbons and oxygen are flammable between given compositions. The feed compositions cited in this invention are outside the flammability limits for the cited hydrocarbons. In all cases, the feed compositions are on the fuel-rich side of the upper flammability limit. The compositions range from 2 to 16 times the stoichiometric fuel to oxygen ratios for

macroporous with 30 to 80 pores per linear inch. The pores should yield a tortuous path for the reactants and products such as is found in foam ceramics. Straight channel extruded ceramic or metal monoliths yield suitable flow dynamics only if the pore size is very small with >80 pores per linear inch.

The preferred catalyst of the present invention consists essentially of platinum modified with Sn or Cu (a mixture of Sn and Cu may be used) supported on a ceramic foam monolith, preferably on zirconia or α-alumina. The platinum should be deposited on the surface of the ceramic to a loading of 0.2 to 90 wt. %, preferably 2 to 10 wt. %, and more preferably in the absence or substantial absence of palladium, rhodium, and gold. It has been found that palladium causes the catalyst to coke up and deactivate very quickly and thus should be excluded in any amount that is detrimental to the effectiveness of the catalyst. Though rhodium does not lead to catalyst deactivation the product distribution is less favorable.

Preferably the Pt and modifying Sn or Cu is supported on an α-alumina or zirconia ceramic foam monolith with 30 to 80 pores per linear inch, 50 to 90% void fraction, created in such a way to yield a tortuous path for reactants. The Pt and modifiers may be supported on a ceramic foam monolith comprised of any combination of α-alumina, zirconia, titania, magnesium, calcium oxide, or halium oxide such that the support is stable up to 1100°C and does not undergo detrimental phase separation that leads to loss in catalyst integrity.

In addition to Sn and Cu, several other metals were evaluated as modifiers. Pt/Ag exhibited comparable conversion and C₂H₄ selectivity to Pt alone. Experiments using Ag
As the diluent is reduced and as the reactants are preheated, the flammability limits widen, but it is under these conditions that higher fuel to oxygen ratios (further from the flammable range) are preferred. This preference is based on catalyst performance with the extra measure of safety an added benefit.

Under the conditions of the present process, olefin cracking, CO disproportionation and reverse steam reforming of carbon can occur, and may lead to coke formation. It has been found by varying the catalyst contact time, the amount of time allowed for these secondary reactions can be controlled. At higher flow rates the olefin products spend less time in contact with the catalyst and higher olefin selectivities and less coking are observed.

The present invention discloses the catalytic oxidative dehydrogenation of hydrocarbons in an auto thermal reactor at millisecond contact time. High yields of mono-olefins are obtained with a catalyst contact time ranging from 0.1 to 20 milliseconds when using a ceramic foam monolith of 50 to 90% porosity and 0.2 to 1 cm in depth. Under operating conditions, this corresponds to GHSV of 60,000 to 3,000,000 hr⁻¹.

The flow rates are in the range of 60,000–10,000,000 hr⁻¹ GHSV, preferably in the range of 300,000 up to 3,000,000 hr⁻¹ GHSV may be used.

Under the conditions of the present process it can be determined that several reactions may occur namely (1) complete combustion (strongly exothermic); (2) partial oxidation to syngas (exothermic); (3) oxidative dehydrogenation (exothermic); (4) dehydrogenation (endothermic) and cracking (endothermic).

The overall process can be carried out auto thermally. The heat produced by exothermic reactions provides the heat for endothermic reactions. The process does not require the addition of heat.

However, improved results are obtained when moderate amounts of heat are supplied to the system. Preheating the feed shifts the product distribution from the more exothermic reactions (combustion and partial oxidation) to the less exothermic (oxidative dehydrogenation) and endothermic (dehydrogenation and cracking) reactions. Since oxygen is the limiting reactant, this shift improves the process conversion. The selectivity is improved since the less exothermic and endothermic reactions are the desired reactions.

EXAMPLES

The reactor used in the following examples consisted of a quartz tube with an inside diameter of 18 mm containing the catalytic monolith which was sealed into the tube with high temperature alumina-silica cloth that prevented bypass of the reactant gases around the edges of the catalyst. To reduce radiation heat loss and better approximate adiabatic operation, the catalyst was immediately preceded and followed by inert alumina extruded monolith heat shields. The outside of the tube near the reaction zone was insulated.
exothermic and endothermic reactions and the heat losses from the reactor.

Although the process in steady state is auto thermal with feed gases at room temperature, heat was supplied initially to ignite the reaction. A mixture of hydrocarbon air and near the stoichiometric composition for production of synthesis gas was fed to the reactor, and the reactants were heated to the heterogeneous ignition temperature (~230°C for C₂ to C₄ hydrocarbons). After light-off, the external heat source was removed (unless feed preheating is indicated), the reaction parameters were adjusted to the desired conditions, and steady state was established (~10 min) before analysis. For situations where the catalyst was not ignited with a mixture of alkane and oxygen, e.g. Ag as a modifier, a NH₃/O₂ was used for light-off and NH₃ was then gradually exchanged for the alkane. Data shown were reproducible for time periods of at least several hours and on several catalyst samples.

For C₅H₄ oxidation, the major products over all catalysts were C₅H₆, CO, CO₂, CH₃OH, and H₂O. Traces of C₅H₅, C₅H₆, C₅H₈, and C₅H₉ were observed, usually with selectivities <2%. The conversions of oxygen were always above 97%, so reactions again go to completion.

Example 1

Ethane

Pt, Pt/Sn and Pt/Cu Catalysts

FIGS. 1, 2, and 3 show the C₂H₆ conversion, C₂H₄ selectivity, and C₂H₆ yield for oxidative dehydrogenation of ethane over Pt, Pt/Sn (Sn:Pt=7:1), and Pt/Cu (Cu:Pt=1:1) as a function of the feed composition (2.0 is the ethylene stoichiometric ratio). With increasing feed composition, the conversion increased while the selectivity increased over the three catalysts. The addition of Sn significantly enhanced both the conversion (by 7%) and the selectivity (by 5%), which produced the highest C₂H₄ yield of 57% at 25°C. Feed in this study. The Pt/Cu also showed higher conversion and higher selectivity than Pt, the maximum yield being 55%. As shown in FIGS. 4, 5, 6, and 7, both Pt/Sn and Pt/Cu showed 5-9% lower CO selectivity and 1-2% higher CO₂ selectivity than Pt. Among minor products, more C₂H₄ and C₂H₆ were formed on both Pt/Sn and Pt/Cu than on Pt. The addition of Sn or Cu inhibited CO production and promoted the formation of olefins and acetylene without significant change in CH₄ selectivities.

The reaction temperatures decreased from 1000 to 900°C as the C₂H₄/O₂ ratio increased from 1.5 to 2.1 and temperatures were same to within ±20°C on these three catalysts.

No deactivation or volatilization of the catalysts were observed for several hours. No significant coke formation on the catalysts was observed.

Example 2

Ethane

Loadings of Pt, Sn. and Cu

FIG. 8 shows plots of C₂H₆ conversion and C₂H₄ selectivity as functions of Sn/Pt ratio at a feed near the oxidative dehydrogenation stoichiometry (C₂H₄/O₂=1.9). The conversion increased with increased Sn/Pt ratio. On the other hand, the addition of a small amount of Sn (Sn/Pt=1:1) enhanced the selectivity significantly and the further addition led to a slight increase in the selectivity.

Pt/Cu (Cu:Pt=1:1) showed comparable results to Pt/Sn, as described above. However, Pt/Cu (Cu/Pt=3:1) could not be ignited in the mixture of C₂H₆ and O₂. A NH₃/O₂ mixture was used for ignition, but the catalyst extinguished upon exchange of NH₃ for C₂H₆.

A sample of 5 wt% Pt was nearly identical to 2 wt% Pt, although the C₂H₆ conversion was 1% lower with 5 wt% loading. The addition of Sn to 5 wt% Pt also enhanced both the conversion and C₂H₄ selectivity. The 5 wt% Pt/Sn (Sn/Pt=1:1) exhibited comparable results (1% higher conversion and 1% lower selectivity to 2 wt% Pt/Sn (Sn/Pt=1:1). This fact confirms that Sn acts as a promoter for ethane oxidation, regardless of Pt loadings. Neither 5 wt% Pt/Cu (Cu/Pt=1:1) the 2 wt% Pt/Cu (Cu/Pt=3:1) worked autothermally.

Example 3

Preheat

FIG. 9 shows the effect of preheat on the conversion, selectivity, and yield over Pt/Sn (7:1) catalyst at CH₃O₂=1.0. Preheating of reaction gases to 400°C increased the conversion from 77 to 80% and decreased the selectivity from 69 to 65%, which led to an increase in yield from 53 to 58%.

Example 4

n-Butane

Oxidative dehydrogenation of n-butane was examined over Pt, Pt/Sn (Sn:Pt=3), and Pt/Cu (Cu:Pt=1). Both Pt/Sn and Pt/Cu showed much higher C₅H₈ conversion by ~16% than Pt as a function of feed composition (FIG. 10). On the three catalysts, the selectivities to C₂H₄ and CO₂ decreased and selectivity to C₂H₆ increased with increasing C₅H₁₀/O₂ ratio. The C₂H₄ selectivity was only 3-5% and increased slightly with increasing C₅H₁₀/O₂ ratio. The C₂H₄ selectivity from n-C₅H₁₀ was much higher on Pt/Sn and Pt/Cu than on Pt, while the C₂H₆ selectivity was much lower on Pt/Sn and Pt/Cu than on Pt.

Example 5

i-Butane

Oxidation of i-butane was similar to n-butane. Both Pt/Sn (Sn:Pt=3) and Pt/Cu (Cu:Pt=1) showed much higher conversion (by 15-25%) than Pt (FIG. 11). With i-C₅H₁₀, the dominant olefins are i-C₂H₄ (~30%) and C₂H₆ (~30%), on all three catalysts, selectivities to C₂H₆ decreased and selectivities to C₂H₄ and i-C₂H₄ increased with increasing C₅H₁₀/O₂ ratio. As a function of conversion, Pt/Sn and Pt/Cu exhibited higher selectivities to olefins and acetylene than Pt at high conversion.

XRD

X-ray diffraction patterns were determined for Pt and Pt/Sn (Sn:Pt=1:1 and 7:1) catalysts after reaction. On Pt catalyst, only peaks of Pt metal were observed except for that of the α-Al₂O₃ support. On the other hand, only PtSn and PtSn peaks were observed for Pt/Sn catalysts and there were no Pt metal peaks. The PtSn/PtSn ratio was higher for Pt/Sn (1:7) than for Pt/Sn (1:1). These results clearly indicate that Pt exists in the forms of only PtSn and PtSn alloys on support for Pt/Sn catalyst.

The addition of Sn or Cu to Pt-monolith enhanced alkane conversion and olefin selectivities and suppressed CO₂ formation for the oxidative dehydrogenation reactions. Since Pt exists in the forms of only PtSn and PtSn alloys on PtSn
catalyst, it is speculated that PtSn and Pt,Sn alloys are the active sites and are more selective to C2H4 formation that Pt.

The invention claimed is:

1. A process for the production of a mono-olefin from a gaseous paraffinic hydrocarbon having at least two carbon atoms or mixtures thereof, the method comprising contacting said hydrocarbon or mixture of hydrocarbons with molecular oxygen under auto thermal oxidative dehydrogenation conditions in the presence of a platinum catalyst supported on a ceramic monolith to produce the corresponding olefins, wherein the platinum catalyst consists essentially of platinum alloyed with tin in an atomic ratio of Sn:Pt of 0.5:1 to 7:1.

2. The process according to claim 1 wherein the ceramic monolith comprises alumina or zirconia.

3. The process according to claim 1 wherein platinum is present in an amount of 0.2 wt % to 10 wt %, based on the total weight of the ceramic monolith and platinum catalyst.

4. The process according to claim 1 wherein the gaseous paraffin and said oxygen have a flow rate in a range of 60,000 to 10,000,000 hr⁻¹ GHSV.

5. The process according to claim 1 wherein the gaseous paraffin and said oxygen have a flow rate in a range of 600,000 to 3,000,000 hr⁻¹ GHSV.

6. The process according to claim 1 wherein the gaseous paraffinic hydrocarbon or mixture of hydrocarbons having at least two carbon atoms comprises an alkane or mixture of alkanes having two to twenty carbon atoms.

7. The process according to claim 6 wherein the alkane or mixture of alkanes have two to eight carbon atoms.

8. The process according to claim 7 wherein the alkane is selected from the group of ethane, propane, n-butane, isobutane, n-pentane, isopentanes, n-hexane, isohexanes, n-heptane, isohexane, octane, isoocotanes, and mixtures thereof.

9. The process according to claim 8 wherein the alkane or mixture of alkanes comprises ethane.

10. The process according to claim 8 wherein the alkane or mixture of alkanes comprises propane.

11. The process according to claim 8 wherein the alkane or mixture of alkanes comprises n-butane.

12. The process according to claim 8 wherein the alkane or mixture of alkanes comprises isobutane.

13. The process according to claim 1 wherein the paraffinic hydrocarbon or mixture of hydrocarbons and molecular oxygen are initially heated to a temperature in a range of 25⁰ C. to 400⁰ C.

14. The process according to claim 1 wherein the ceramic monolith is a foam ceramic monolith.

15. The process according to claim 1 wherein the mixture of hydrocarbons and molecular oxygen has a feed composition from 2 to 16 times the stoichiometric fuel to oxygen ratios for combustion to CO₂ and H₂O.

16. A process for the production of corresponding olefins, the method comprising feeding a gaseous alkane or mixture of alkanes having two to twenty carbon atoms and molecular oxygen under auto thermal oxidative dehydrogenation conditions to a catalyst consisting essentially of platinum alloyed with tin supported on a ceramic foam monolith.

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