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Vajda et al.

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(54) **SELECTIVE OXIDATION OF PROPANE TO PROPYLENE OXIDE**

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C07D 305/06	(2006.01)
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B01J 35/00	(2006.01)
B01J 23/89	(2006.01)
B01J 21/04	(2006.01)
B01J 23/72	(2006.01)

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CPC ***C07D 305/06*** (2013.01); ***B01J 21/04*** (2013.01); ***B01J 23/44*** (2013.01); ***B01J 23/72*** (2013.01); ***B01J 23/8926*** (2013.01); ***B01J 35/0006*** (2013.01)

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USPC 549/510
See application file for complete search history.

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Wentao Wei et al., One-Pot Synthesis, Photoluminescence, and Electrocatalytic Properties of Subnanometer-Sized Copper Clusters, Journal of the American Chemical Society, Jan. 31, 2011, vol. 133, pp. 2060-2063.

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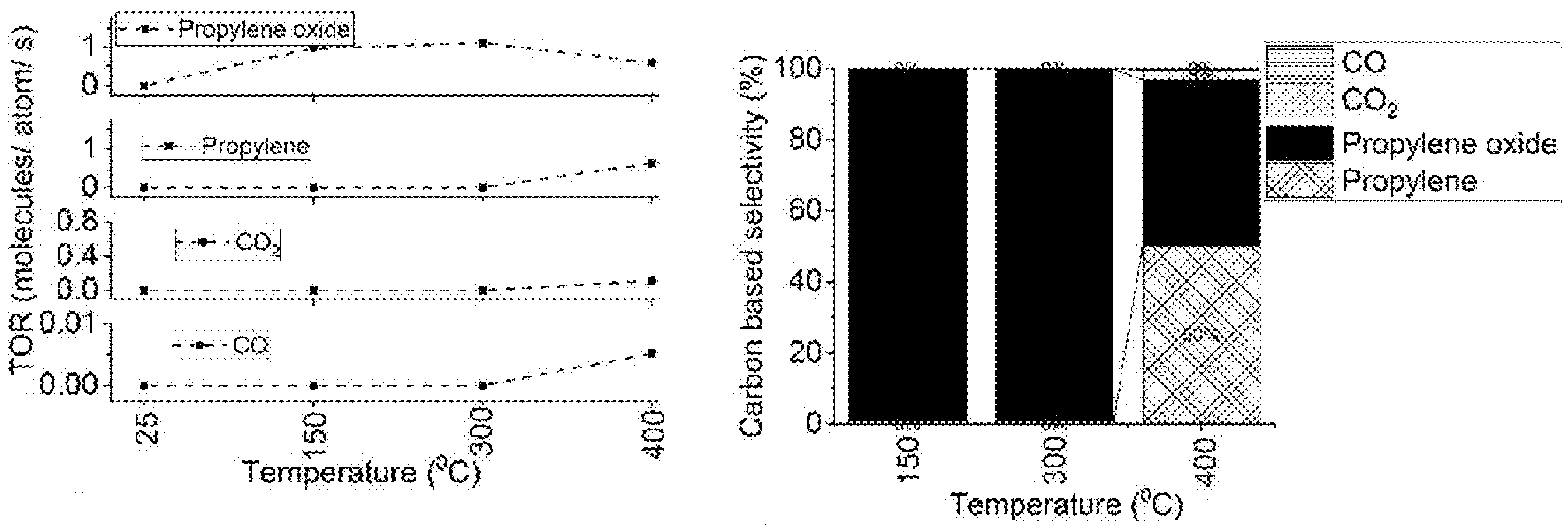
(57) **ABSTRACT**

The invention provides a one pot method for generating propylene oxide, the method having the steps of contacting propane with catalyst clusters no greater than 30 atoms in the presence of oxygen for a time sufficient to directly convert the propane to the propylene oxide. The invented method eliminates the generation of intermediate compounds or intermediate reaction steps.

19 Claims, 7 Drawing Sheets



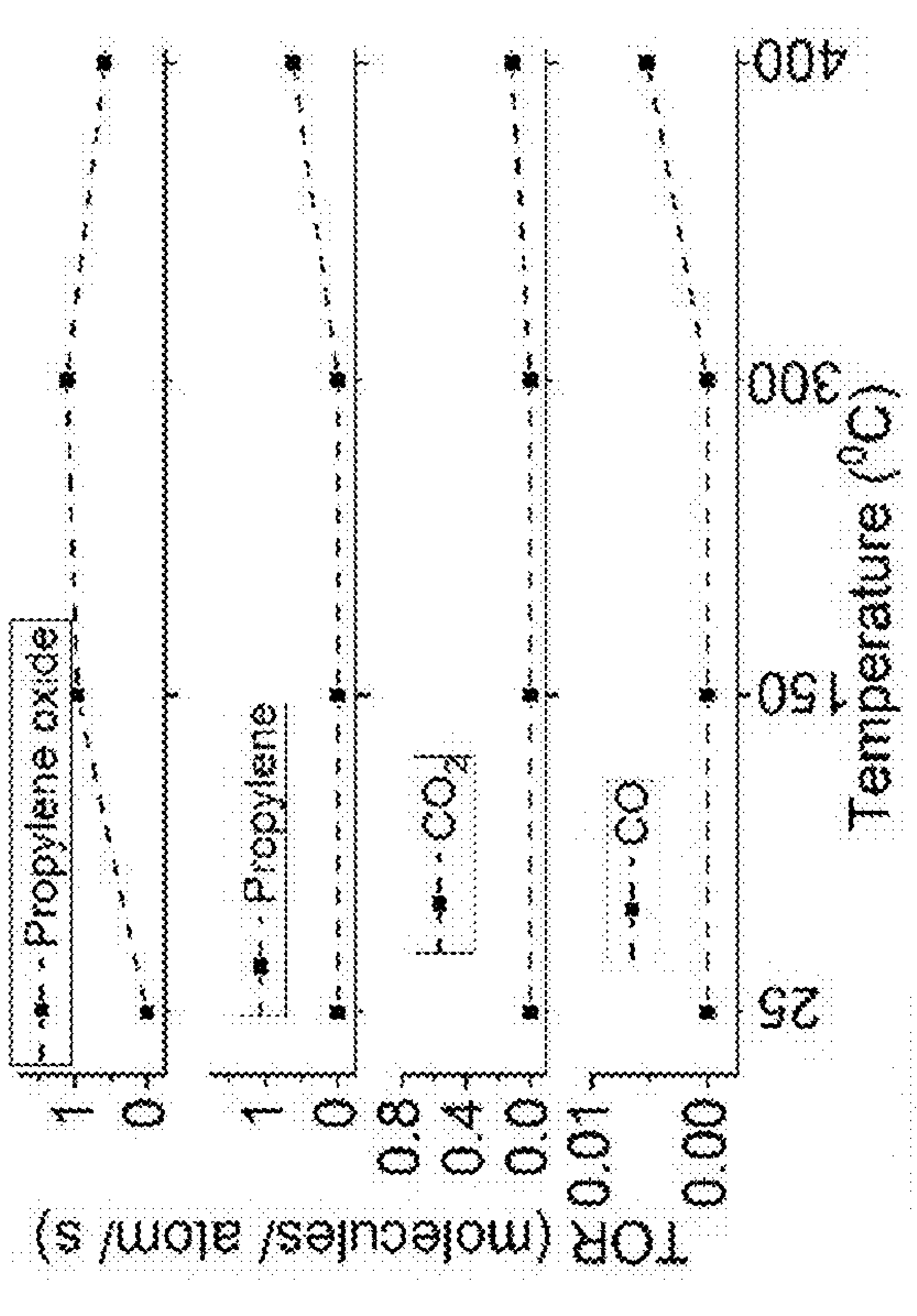

TOR (molecules/ atom/ s)
Propylene oxide
1
0
Propylene
1
0
CO$_2$
0.8
0.4
0.0
CO
0.01
0.00
25
150
300
400
Temperature (°C)

FIG. 1A

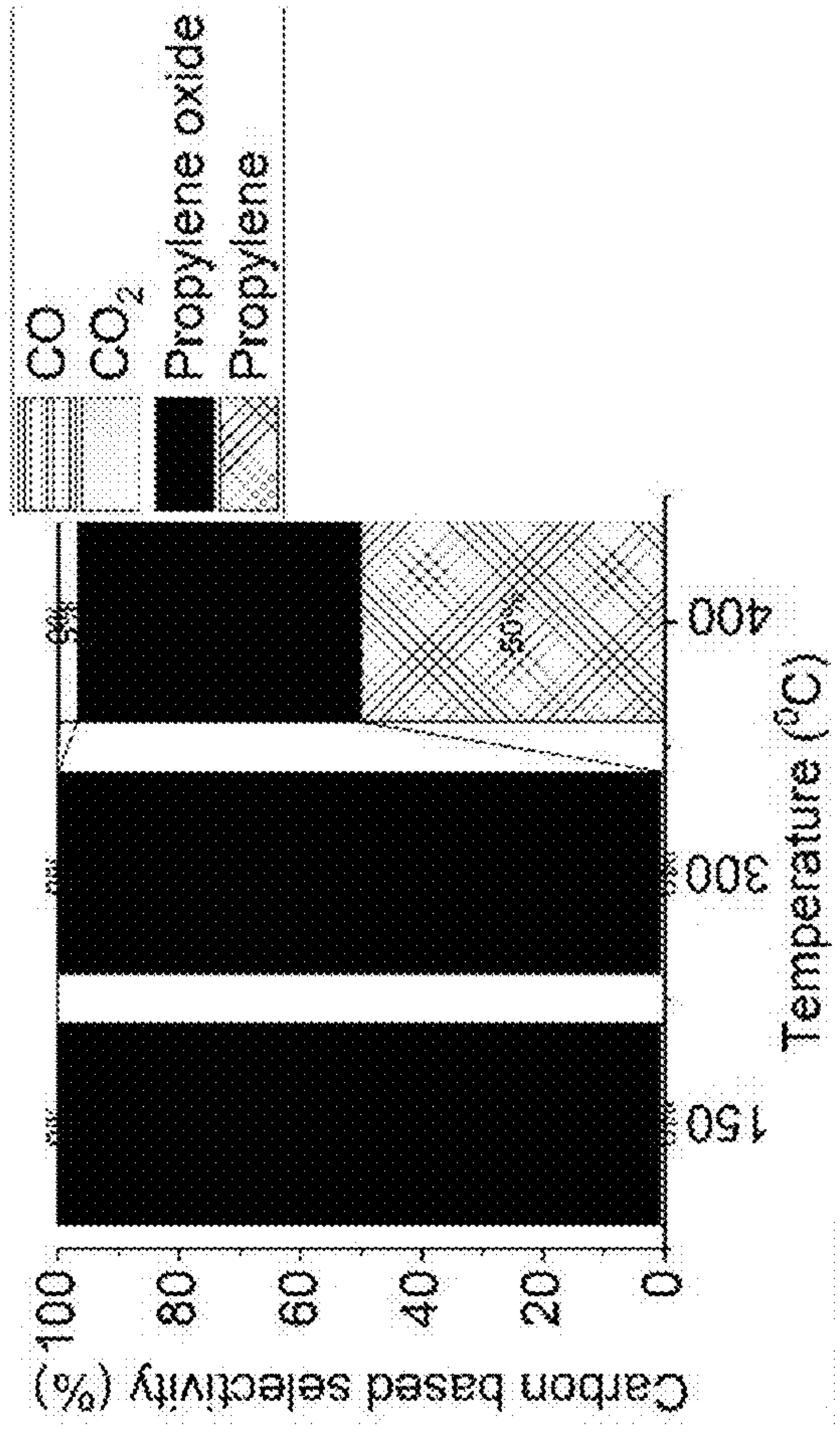

Carbon based selectivity (%)
100
80
60
40
20
0
150
300
400
Temperature (°C)
50%
CO
CO$_2$
Propylene oxide
Propylene

FIG. 1B

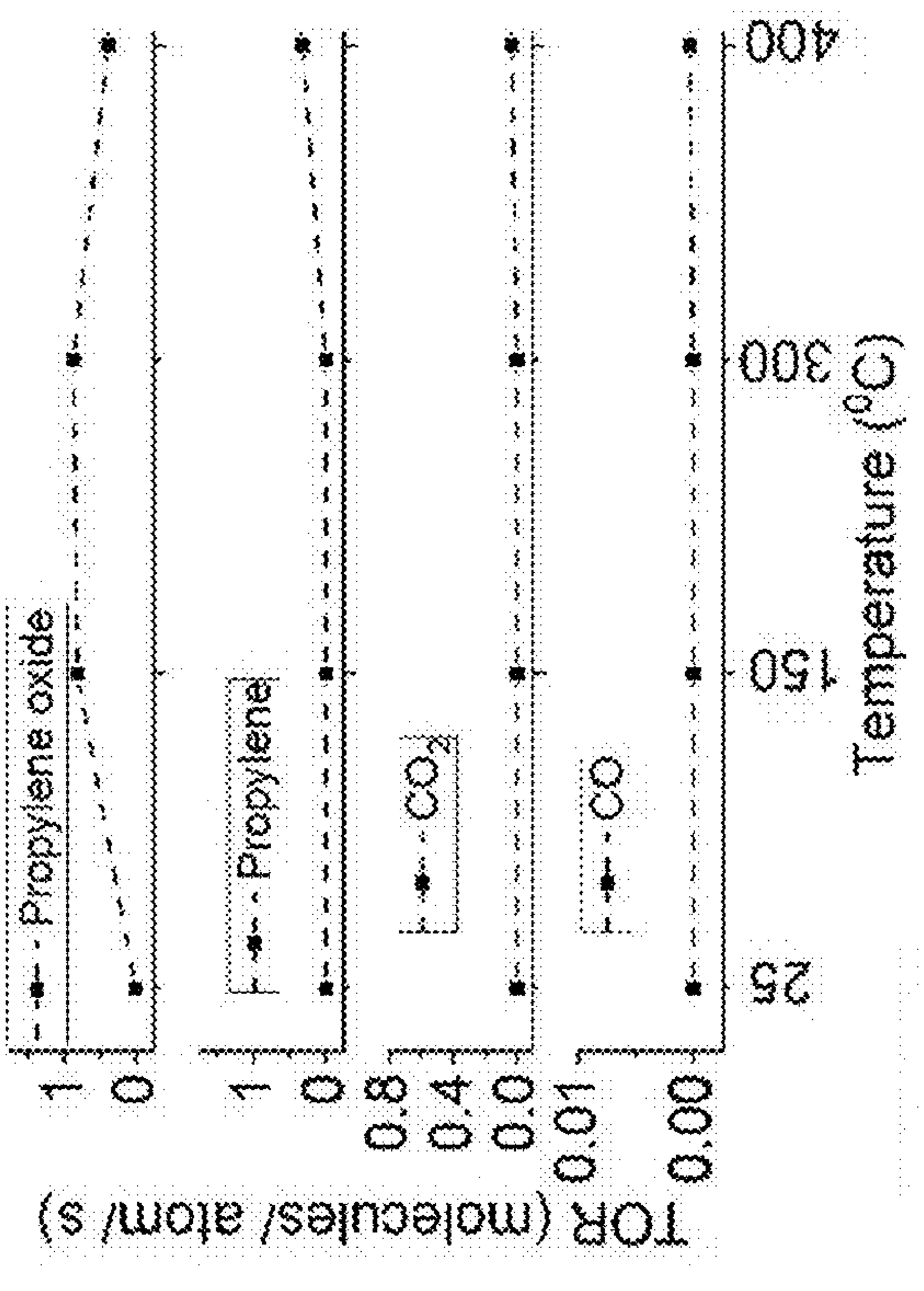

TOR (molecules/ atom/ s)
1
0
1
0
0.8
0.4
0.0
0.01
0.00
Propylene oxide
Propylene
CO_2
CO
25
150
300
400
Temperature (^{0}C)

FIG. 2A

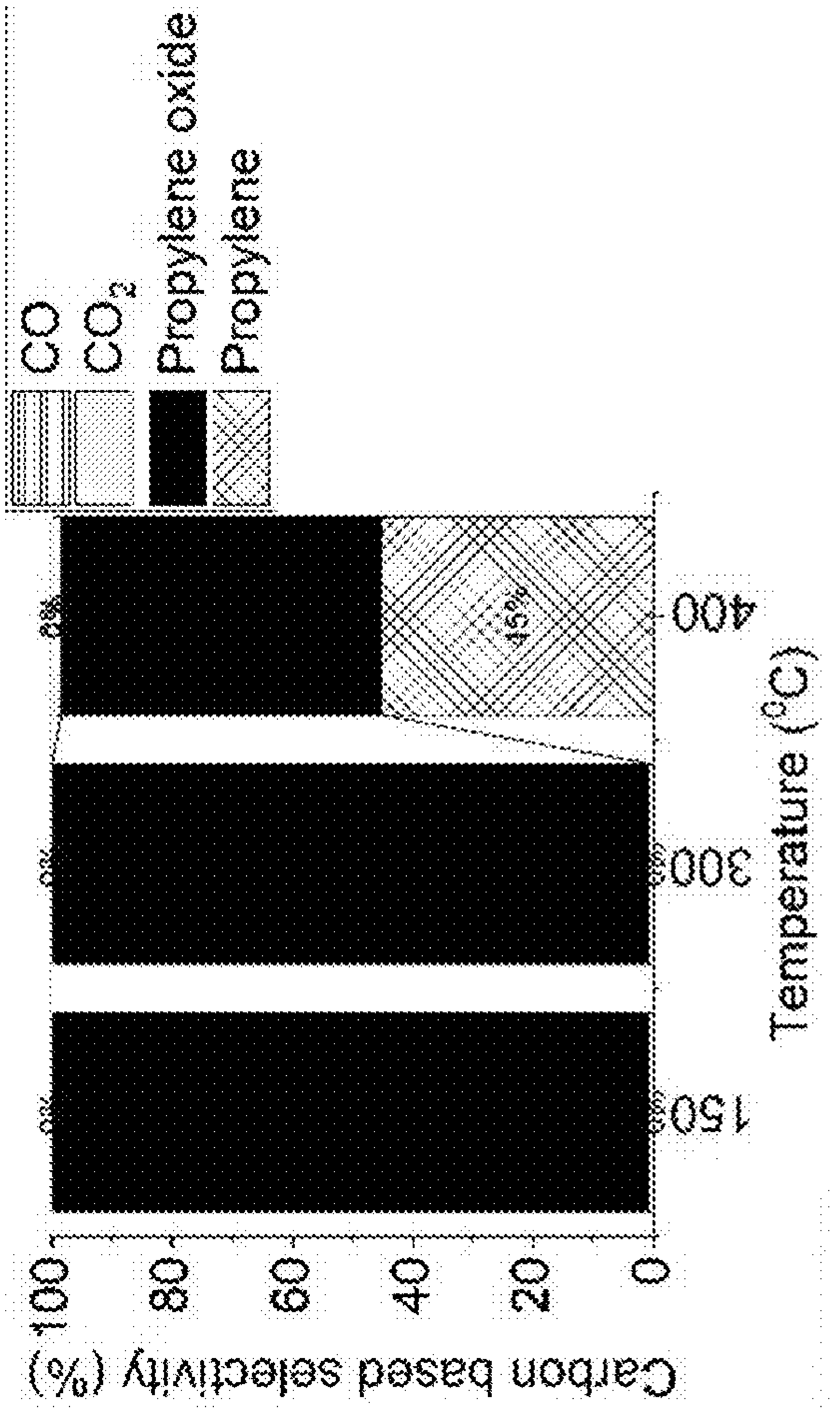

Carbon based selectivity (%)
100
80
60
40
20
0
45%
150
300
400
Temperature (^{0}C)
CO
CO_2
Propylene oxide
Propylene

FIG. 2B

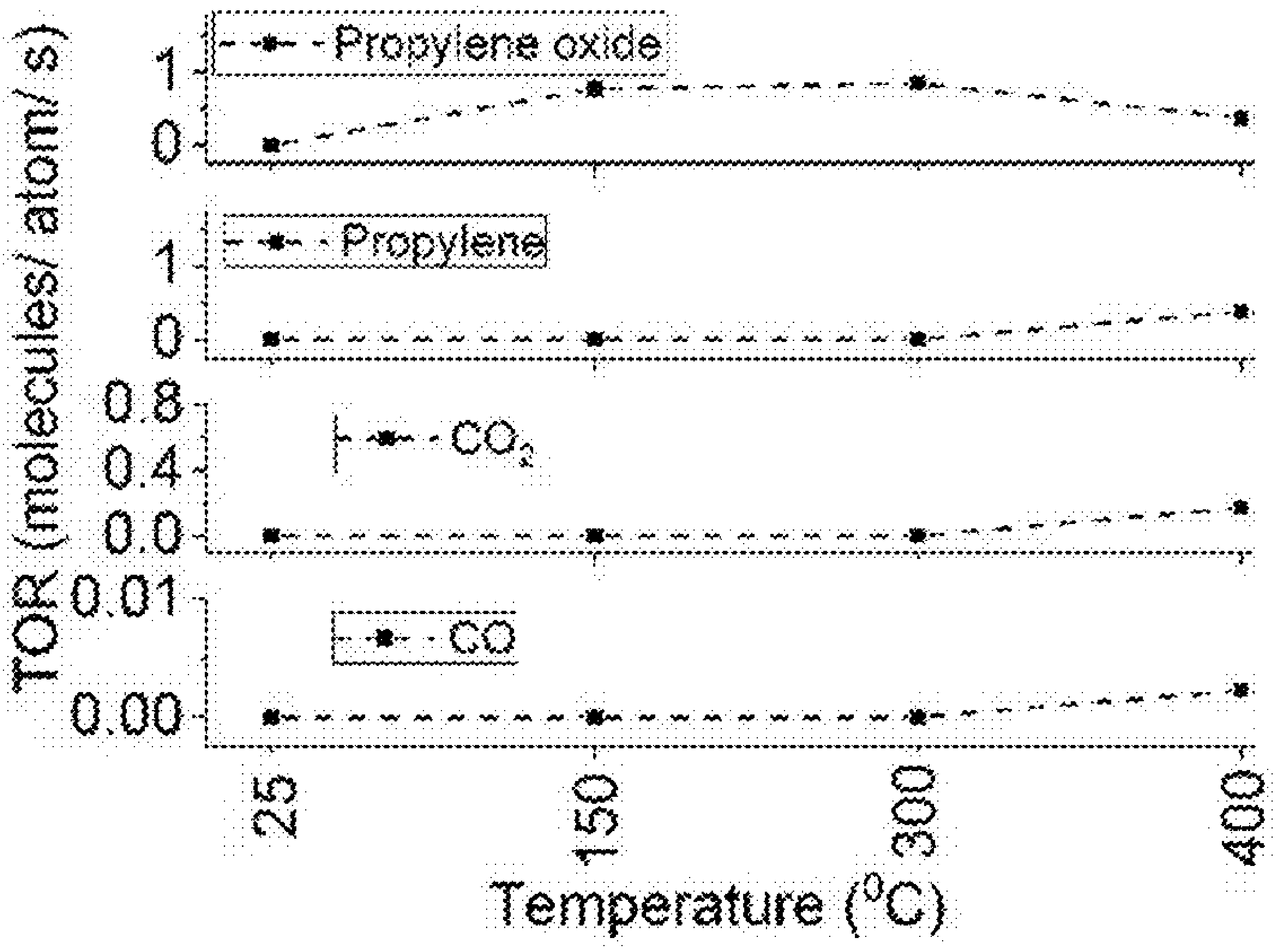

TOR (molecules/ atom/ s)
Propylene oxide
Propylene
CO_2
CO
1
0
0.8
0.4
0.0
0.01
0.00
25
150
300
400
Temperature (°C)

FIG. 3A

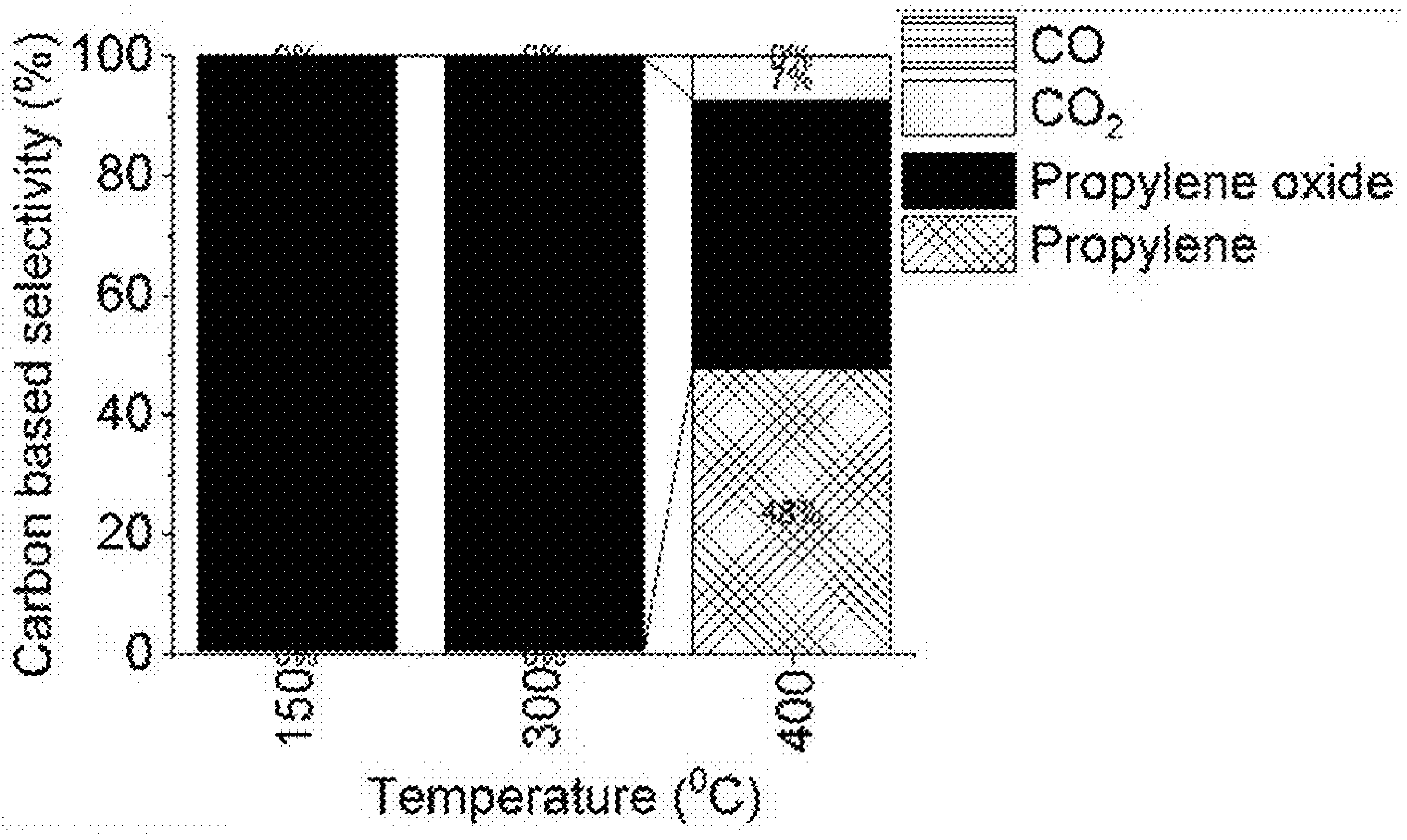

Carbon based selectivity (%)
100
80
60
40
20
0
150
300
400
Temperature (°C)
0%
7%
48%
CO
CO_2
Propylene oxide
Propylene

FIG. 3B

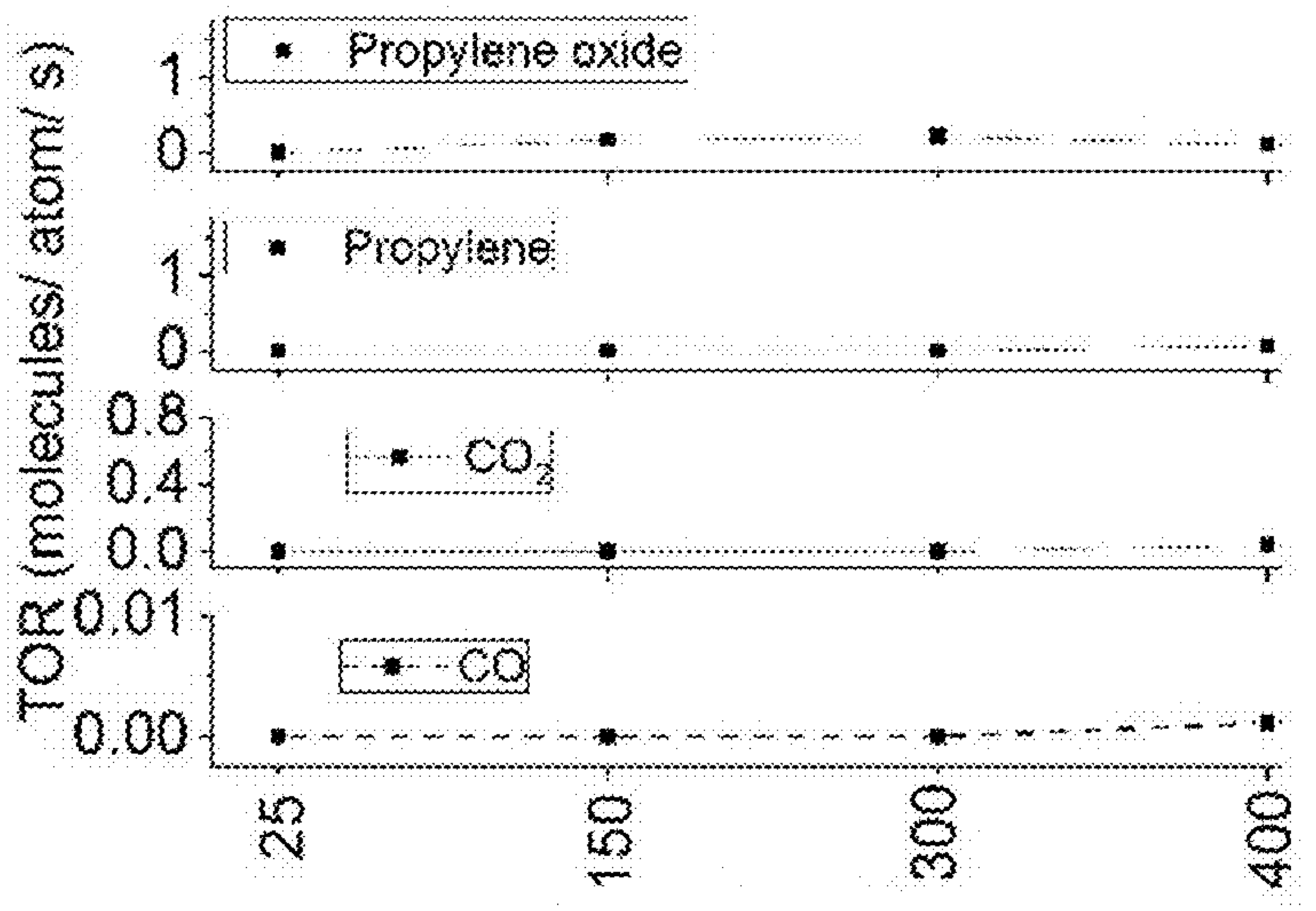

TOR (molecules/ atom/ s)
Propylene oxide
Propylene
CO_2
CO
1
0
1
0
0.8
0.4
0.0
0.01
0.00
25
150
300
400

FIG. 4A

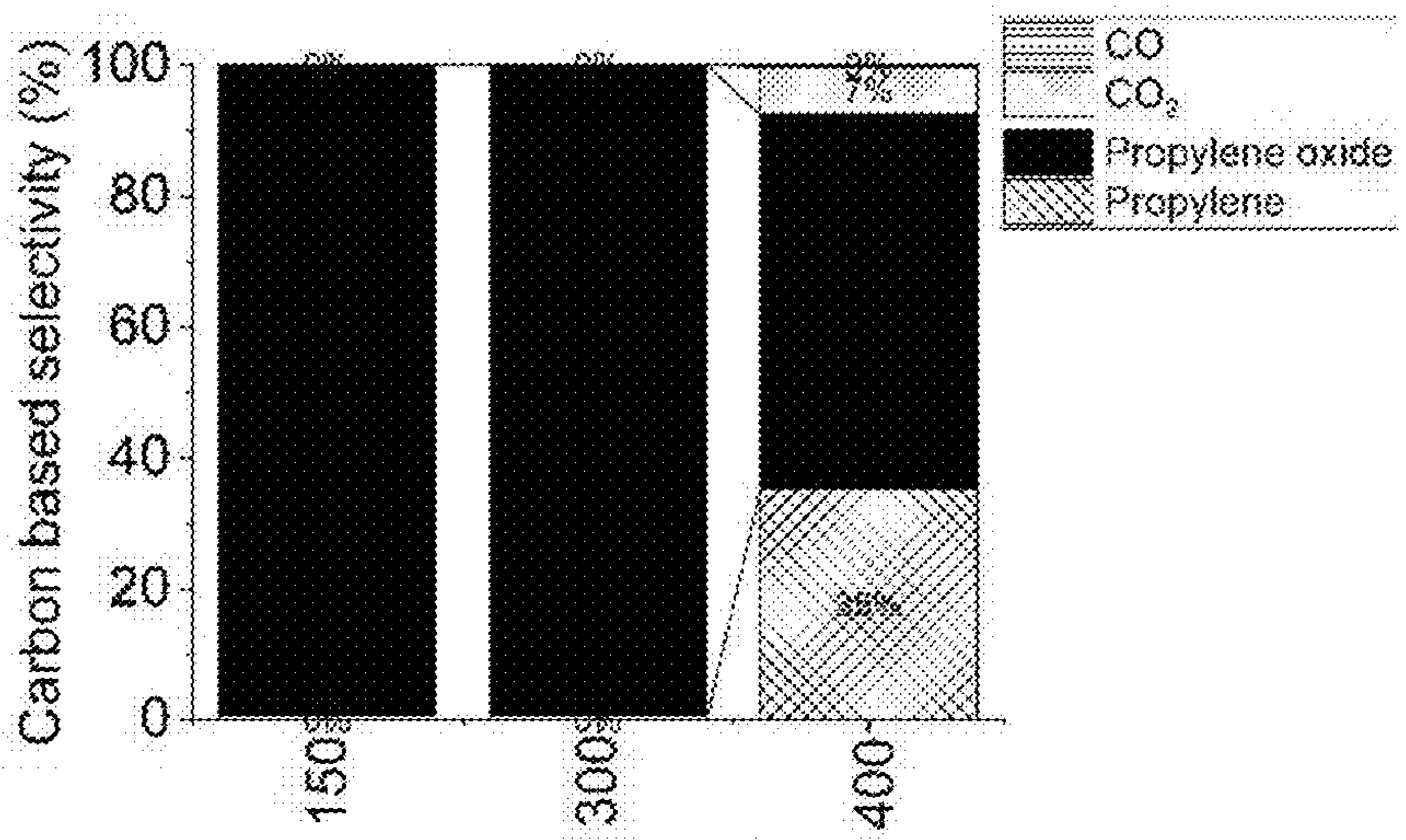

Carbon based selectivity (%)
100
80
60
40
20
0
150
300
400
7%
35%
CO
CO_2
Propylene oxide
Propylene

FIG. 4B

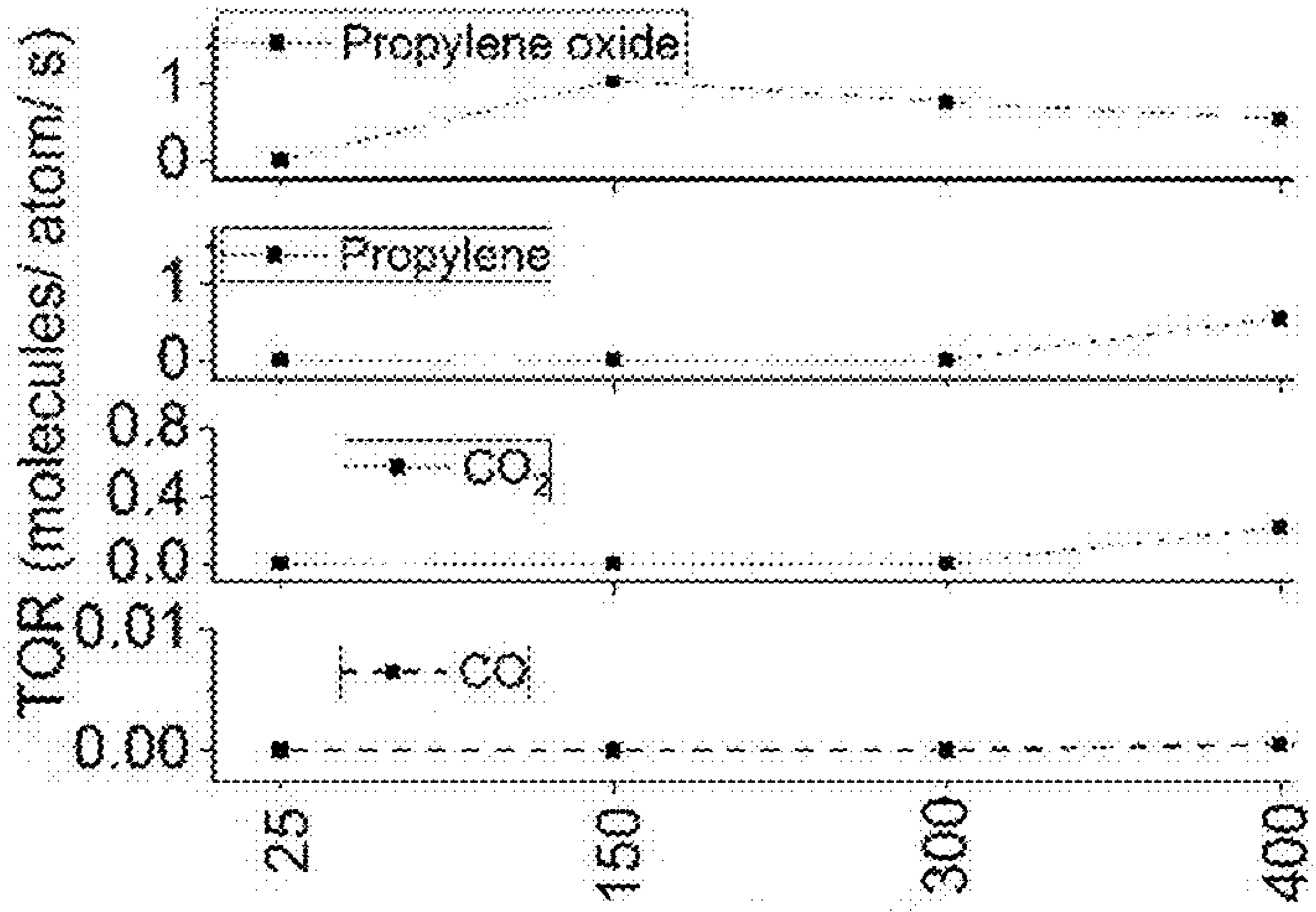

TOR (molecules/ atom/ s)
Propylene oxide
1
0
Propylene
1
0
0.8
0.4
0.0
CO_2
0.01
0.00
CO
25
150
300
400

FIG. 5A

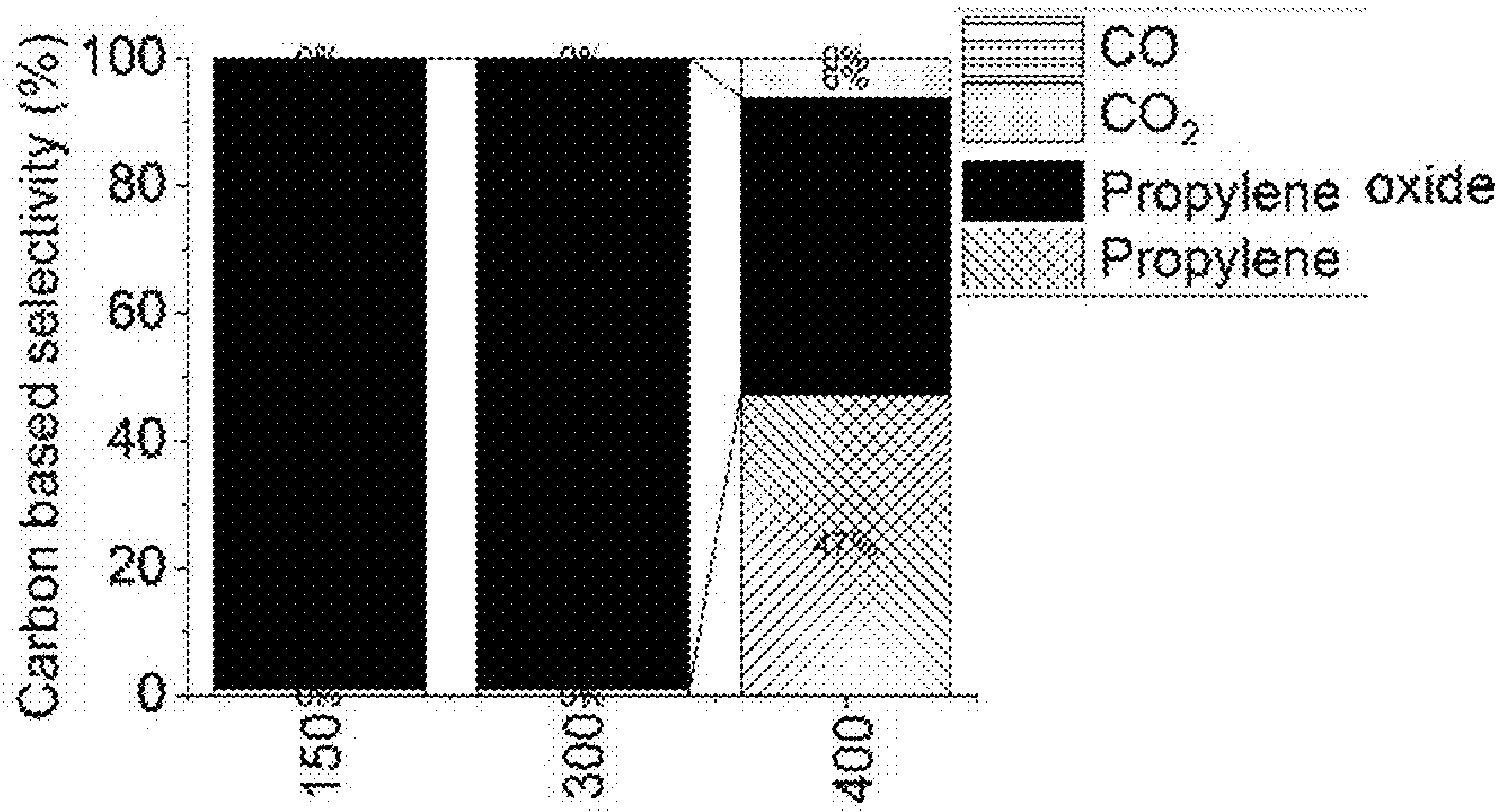

Carbon based selectivity (%)
100
80
60
40
20
0
0%
0%
0%
6%
47%
150
300
400
CO
CO_2
Propylene oxide
Propylene

FIG. 5B

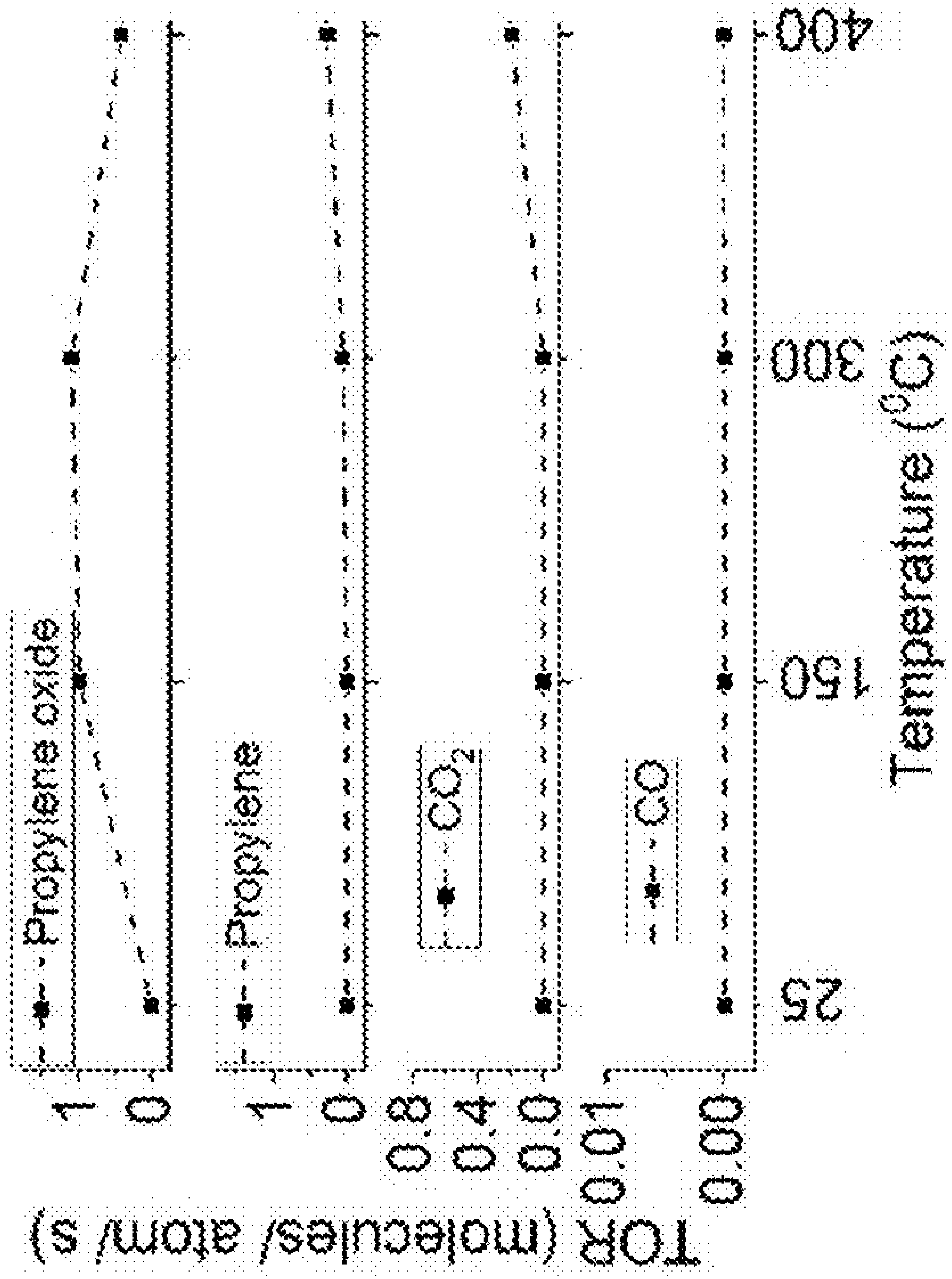

TOR (molecules/ atom/ s)
Propylene oxide
1
0
Propylene
1
0
CO$_2$
0.8
0.4
0.0
CO
0.01
0.00
25
150
300
400
Temperature (°C)

FIG. 6A

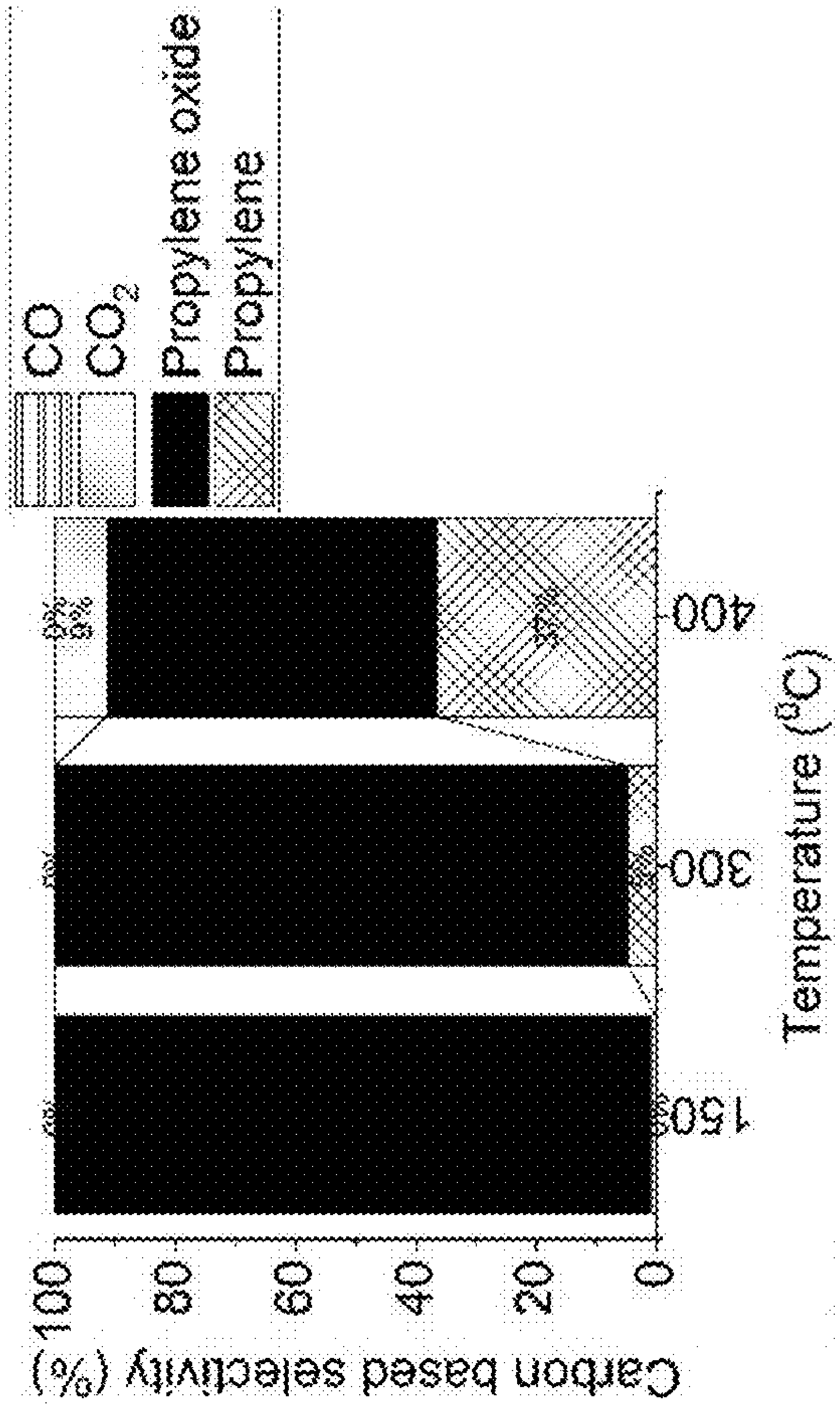

Carbon based selectivity (%)
100
80
60
40
20
0
150
300
400
Temperature (°C)
CO
CO$_2$
Propylene oxide
Propylene

FIG. 6B

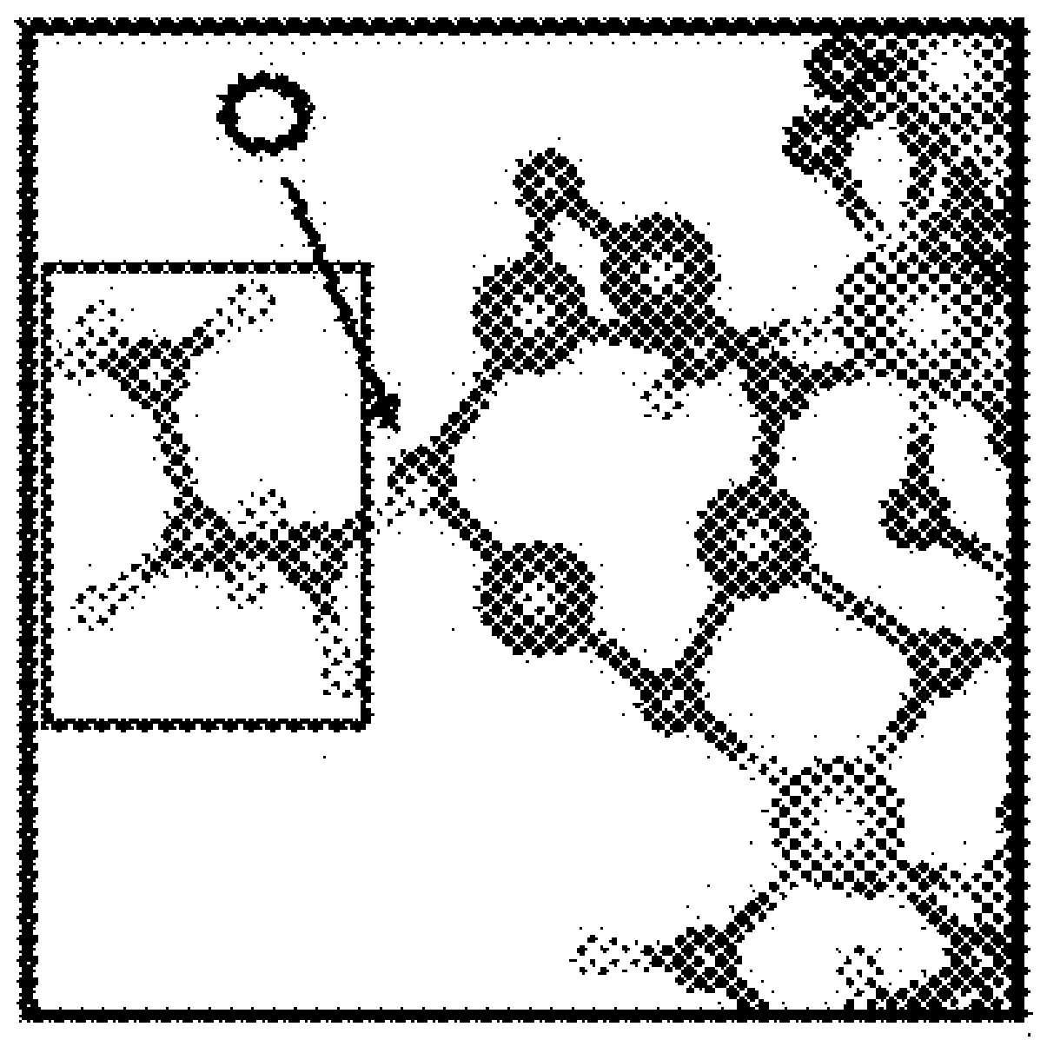


FIG. 7A

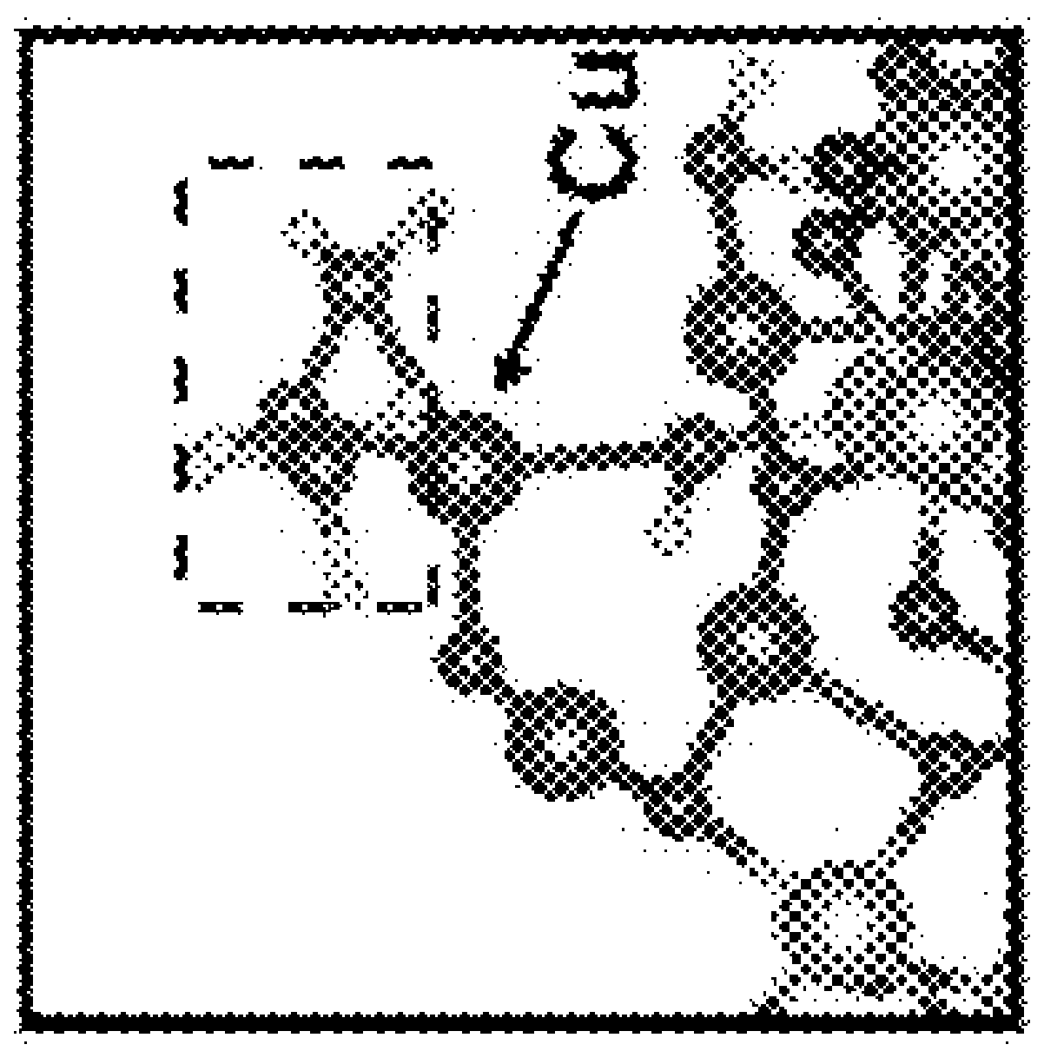


FIG. 7B

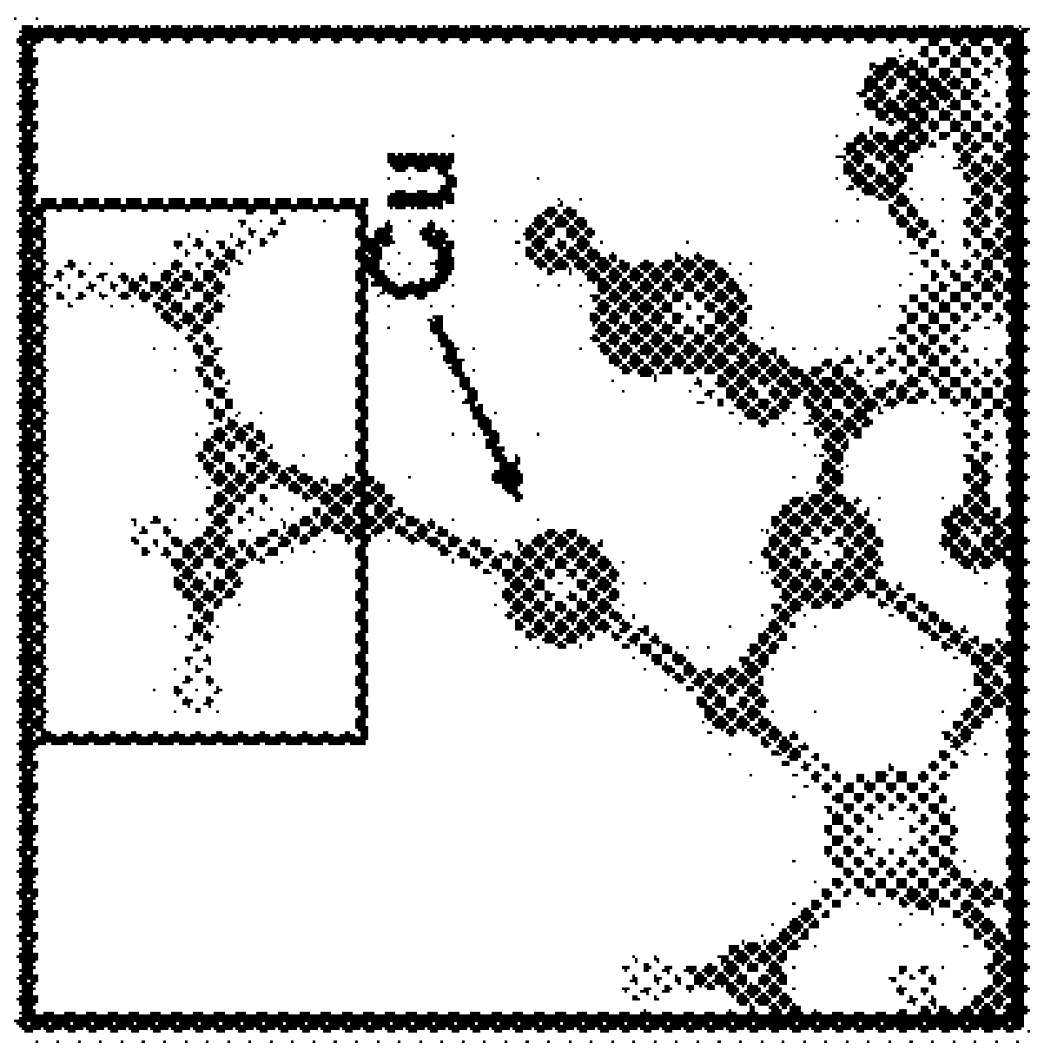


FIG. 7C

SELECTIVE OXIDATION OF PROPANE TO PROPYLENE OXIDE

CONTRACTUAL ORIGIN OF THE INVENTION

This invention was made with government support under Contract No. DE-AC02-06CH11357 awarded by the United States Department of Energy to UChicago Argonne, LLC, operator of Argonne National Laboratory. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a system and a method for producing propylene oxide and more specifically, this invention relates to a system and method for producing propylene oxide directly from propane.

2. Background of the Invention

Propylene oxide (PO) is a key commodity of the petrochemical industry, produced from propylene, and is used to produce a wide range of consumer products like rigid foams, moldings, adhesive, coatings etc. PO has a present market value of $13 billion and is projected to have a 50% rise by 2023.

A myriad of protocols for producing PO exist, just not directly from propane. Protocols are available for transforming propylene to PO. However, those industrial techniques like chlorohydrin-, hydroperoxide-, cumene-based, and styrene monomer-processes produce abundant side products and side streams.

A current route to produce PO, is by propylene epoxidation or by a two-step conversion from propane. At the first step, propane is dehydrogenated to propylene and H_2. In the next step, the mixture of propylene, propane, and H_2, is co-fed with oxygen and then treated with a suitable catalyst (for e.g. titanium silicate) to form PO. These multi-step processes are resource intensive and time consuming.

At present, there is no process or system for directly converting propane to PO.

A need exists in the art for a single step conversion process of propane to propylene oxide. The process should bypass intermediate product generation, separation, and storage. The process and system should also eliminate the need for complex oxidation routes to produce PO by e.g., hydrogen peroxide or cumene. Rather, the process and system should produce PO at higher efficiencies using lower, cheaper metal loadings, compared to the state of the art processes, and at lower costs.

SUMMARY OF INVENTION

An object of the invention is to provide a system and method for producing propylene oxide that overcomes many of the drawbacks of the prior art.

Another object of the invention is to provide a system and method for efficiently producing propylene oxide. A feature of the invention is utilization of catalysts comprised of specific numbers of atoms. An advantage of the invention is the high activity due to exposing propane feedstock to every atom comprising the conversion catalysts utilized. For example, about 1.2 propylene oxide molecules are produced per metal atom per second at 300° C.

Still another object of the invention is to provide a one pot method for producing PO from propane. A feature of the invention is that nearly 100 percent selectivity to PO from about 150 C and 300° C. (For example, if one propylene oxide molecule is produced for every propane molecule, that represents 100 percent selectivity) An advantage of the invention is elimination of oxidative dehydrogenation of propane (which itself is typically performed at significantly higher temperatures), the elimination of precious metal catalysts or oxide based catalysts, and the elimination of a separation sequence for propene.

Yet another object of the invention is to provide a low temperature, one step process for producing PO. A feature of the invention is that it uses molecular oxygen in an exothermic one-step process. An advantage of the invention is the exothermicity of such oxidative dehydrogenation is much less energy demanding than endothermic non-oxidative dehydrogenation.

Another object of the invention is to provide a low cost process for making propylene oxide. A feature of the invention is the use of highly dispersed metals, i.e. catalysts made of ultra-small particles (clusters) comprising a handful of atoms. These metals may consist of abundant relatively inexpensive elements. An advantage of the invention is that it makes the most efficient and economic use of precious metals and common metals. For example, the invented method generates propylene oxide directly from propane without any intermediate steps or reactions and without first preparing propylene.

Briefly, the invention provides a one pot method for generating propylene oxide, the method comprising contacting propane with catalyst clusters smaller than 1 nanometer in diameter (e.g., 1-30 atoms) in the presence of oxygen for a time sufficient to convert the propane to the propylene oxide.

BRIEF DESCRIPTION OF DRAWING

The invention together with the above and other objects and advantages will be best understood from the following detailed description of the preferred embodiment of the invention shown in the accompanying drawings, wherein:

FIGS. **1**A-**1**B are a series of graphs showing rate of formation (TOR) and selectivity of reaction products using neat 4-atom based copper clusters (Cu_4), in accordance with features of the present invention;

FIGS. **2**A-B are a series of graphs showing rate of formation (TOR) and selectivity of reaction products using neat 12-atom based copper clusters (Cu_{12}), in accordance with features of the present invention;

FIGS. **3**A-**3**B are a series of graphs showing rate of formation (TOR) and selectivity of reaction products using neat 20-atom based copper clusters (Cu_{20}), in accordance with features of the present invention;

FIGS. **4**A-B are a series of graphs showing rate of formation (TOR) and selectivity of reaction products using neat 4 atom palladium clusters Pd_4, in accordance with features of the present invention;

FIGS. **5**A-B are a series of graphs showing rate of formation and selectivity of reaction products using 4-atom copper, 1 atom palladium clusters Cu_4Pd, in accordance with features of the present invention;

FIGS. **6**A-B are a series of graphs showing rate of formation and selectivity of reaction products using 3-atom copper, 1-atom palladium clusters Cu_3Pd, in accordance with features of the present invention; and

FIG. 7A-C are schematic depictions of the interactions of reagent and product molecules to atoms comprising the catalyst cluster, in accordance with features of the present invention.

DETAILED DESCRIPTION

The foregoing summary, as well as the following detailed description of certain embodiments of the present invention, will be better understood when read in conjunction with the appended drawings.

All numeric values are herein assumed to be modified by the term “about”, whether or not explicitly indicated. The term “about” generally refers to a range of numbers that one of skill in the art would consider equivalent to the recited value (e.g., having the same function or result). In many instances, the terms “about” may include numbers that are rounded to the nearest significant figure.

The recitation of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

The following detailed description should be read with reference to the drawings in which similar elements in different drawings are numbered the same. The drawings, which are not necessarily to scale, depict illustrative embodiments and are not intended to limit the scope of the invention.

As used herein, an element or step recited in the singular and preceded with the word “a” or “an” should be understood as not excluding plural said elements or steps, unless such exclusion is explicitly stated. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

Furthermore, references to “one embodiment” of the present invention are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features. Moreover, unless explicitly stated to the contrary, embodiments “comprising” or “having” an element or a plurality of elements having a particular property may include additional such elements not having that property.

The present invention provides a method and system for the efficient conversion of propane to propylene oxide. A salient feature of the invention is the use of clusters comprising mono- and/or bimetallic catalysts to directly convert propane to propylene oxide in the presence of oxygen. The clusters can be as large as 10 nm, but typically are between approximately 0.2 nm and 5 nm in diameter and preferably between 0.3 nm and 7 nm in diameter.

These small clusters can serve as model catalytically active sites with a large fraction of undercoordinated, thus potentially highly active, sites.

The present invention reports a new catalyst to produce PO directly from propane. The invention eliminates the multi-step process of need of 1) producing propylene from propane, 2) oxidizing the produced propylene to PO, and then 3) separating out any residual propylene from the reaction liquor. Since the reported process works with molecular oxygen feed, an efficient activation of oxygen by the reported catalysts occurs during the process.

The invented catalyst facilitates the following reactions:

$$C_3H_8+1/2O_2 \rightarrow C_3H_6+H_2O \qquad \text{Equation 1}$$

$$C_3H_6+1/2O_2 \rightarrow C_3H_6O \qquad \text{Equation 2}$$

A schematic of the above chemistry is depicted in FIGS. 7A-7C, which is discussed infra.

An embodiment comprises a subnanometer cluster based mono- and bi-metallic catalyst made of Cu and Pd that produces propylene oxide directly from propane with high activity and selectivity, in a one-pot (i.e., one reaction vessel) synthesis process. The invention leverages the temperature-dependent catalytic properties of the metal-oxide film-supported monometallic Cu and Pd clusters, as well as bimetallic Cu—Pd clusters.

Metal oxide supports may include those selected from the group consisting of alumina, iron-oxide, silica oxide, zeolites, titanium oxide, zinc oxide, zirconium oxide, tin oxide, magnesium oxide, including their combinations. Carbon based supports selected from the group consisting of nanocrystalline diamond, graphite, amorphous carbon various forms and compositions of graphene may also be utilized, including their combinations. These supports may be modified with oxygen, nitrogen, hydrogen and metal dopants. The supports may define planar or nonplanar surfaces or loose aggregate such as powders.

Ultimately, the supports are exposed to a gas mixture containing propane and oxygen, at near atmospheric pressure.

The conversion occurs at high rates (up to about 1.2 propylene oxide molecules produced per metal atom per second at 300° C.), with suppressed formation of such combustion products as CO and CO_2. Catalyst performance is tunable through cluster-size and cluster-composition.

At higher temperatures the cluster-based process produces propylene, another high volume commodity chemical, at a high rate (up to about 1.6 propylene molecules produced per cluster metal atom per second at 550° C.), with high selectivity (about 80 percent). From the studied Cu, Pd and CuPd cluster compositions, monometallic Cu clusters were found possessing the highest activity as well as selectivity in both propylene oxide and propylene production. Theoretical calculations support the experimentally observed high activity and selectivity of the best performing Cu_4 clusters. No quantifiable acrolein byproduct formation was observed, as anticipated by theoretical calculations which show higher barriers for acrolein production than for PO production.

Reaction Conditions Detail

Oxidative dehydrogenation of propane occurs over different size metal clusters. Reactant gas may comprise pure propane (i.e., neat with typical impurities), or else in a carrier gas. Temperature of the conversion ranges from 150° C. to 300° C. Between temperature steps of 50° C., a slow heating/cooling is applied to assure thermal stabilization. Suitable pressures are from 0.01 atm to 20 atm.

Feedstream components can vary, as long as propane comprises about 0.2 percent or more of the feedstream, and oxygen comprises about 0.05 percent or more of the feedstream. The presence of possible promoters, such as co-fed water, hydrogen, CO_2, N_2O, H_2O_2, O_3, and combinations thereof can be used to further increase efficacy.

Catalyst Preparation

Detail

Small clusters (those containing less than about 30 atoms) comprise catalytically active sites with a large fraction of undercoordinated, thus potentially highly active, sites. These features along with the strong charge transfer with the support material and cluster's fluxionality confers the clusters with features not present within its bulk analog.

A myriad of elemental metals, their alloys and compounds may serve as catalyst material, including but not limited to Cu, Ag, Au Co, Fe, Mo, Pd, Pt, Ti, V, W, their oxides and carbides, and combinations thereof.

The catalysts are prepared by softly landing the clusters which are produced in a molecular beam within a high vacuum chamber on an ALD coated substrate (e.g. alumina) on SiO_2/n-type (P-doped) Si wafer. The clusters are so landed that the impact energy is less than 1 eV per atom which ensures that the clusters stay intact and does not undergo fragmentation or pinning onto the substrate. Soft landing protocols are described in U.S. Pat. No. 8,143,189 B2, issued to the applicant, and incorporated in its entirety herein.

Alternatively, cluster distributions may be prepared by wet methods, such as those methods described in Wentao Wei, Yizhong Lu, Wei Chen, and Shaowei Chen *J. Am. Chem. Soc.,* 2011, 133 (7), pp 2060-2063, the entirety of which is incorporated herein by reference.

Rigid substrates may be metal oxide selected from the group consisting of aluminum oxide, iron oxide, silicium oxide, zeolites, titanium oxide, zinc oxide, zirconium oxide, tin oxide, magnesium oxide, cerium oxide and combinations thereof. The substrate could be further doped with alkali metals. The clusters-catalysts themselves could be doped with alkali atoms as well.

Example 1

Two clusters within two spots of 8 mm diameter were deposited on the top of n-doped silicon wafers coated with a thin layer of alumina. The alumina layer, of about 3 monolayer (ML) thickness, was fabricated by atomic layer deposition. The metal loading of the Cu_4, Cu_{12}, Cu_{20}, Pd_4, Cu_4Pd, and Cu_3Pd samples was 16.2 ng, 16.2 ng, 16.2 ng, 27.2 ng, 18.4 ng, and 19.00 ng respectively, corresponding to a surface coverage of 10 percent of an atomic monolayer equivalent. This ensures the inter-cluster distance of approximately 5-10 nm and inhibits any sintering occurring during the reaction as the catalyst is heated.

The reaction was performed in situ with X-ray characterization to simultaneously monitor the reaction products formation on a mass spectrometer, and to monitor the changes in the oxidation state of the clusters during the course of the reaction. The reactor was maintained at a pressure of 800 Torr with a continuous 18.54 sccm flow of 3% O_2 and 3% propane mixed in helium carrier gas.

Turnover rate (TOR) is defined as the number of product molecules formed per atom of the catalyst per second. TOR for PO production reached 1.2 at 300° C. which matches or is significantly higher than that obtained by the to-date used techniques where, however, propylene or a mixture of propane and propylene are used as the starting gases.

FIG. **1**A depicts the TOR for propylene, CO and CO_2 for neat 4-atom copper clusters (Cu_4). FIG. **1**B depicts the carbon based selectivity for the reaction products for 4-atom clusters.

FIG. **2**A depicts the TOR for propylene, CO and CO_2 for neat 12-atom copper clusters (Cu_{12}). FIG. **2**B depicts the carbon based selectivity for the reaction products for 12-atom clusters.

FIG. **3**A depicts the TOR for propylene, CO and CO_2 for neat 20-atom copper clusters (Cu_{20}). FIG. **3**B depicts the carbon based selectivity for the reaction products for 20-atom clusters.

The TORs obtained for the larger Cu clusters featured in FIGS. **2**A-B and **3**A-**3**B (Cu_{12}, and Cu_{20} atoms) are comparable to those observed for Cu_4 clusters. This relaxes the specific size requirement for high activity of the catalysts, therefore providing a means for large scale production using alternative techniques, including catalysts prepared by "wet-chemistry."

This data shows 100 percent selectivity for propylene oxide at 150° C. and 300° C., which is to say no combustion products or unwanted moieties are generated.

Example 2

FIGS. **4**A, **4**B, **5**A, **5**B, **6**A, and **6**B depict the formation rate of propylene oxide per metal atom and selectivity on neat 4-atom Pd catalyst clusters (FIGS. **4**A-**4**B) and Cu—Pd catalyst clusters (FIGS. **5**A, **5**B, **6**A, and **6**B).

TOR for propylene, propylene oxide, CO and CO_2 are plotted for 4-atom palladium clusters Pd_4 (FIG. **4**A), 4-atom copper, 1 atom palladium cluster Cu_4Pd (FIG. **5**A), and 3-atom copper, 1-atom palladium cluster Cu_3Pd (FIG. **6**A). Carbon based selectivity for the reaction products are plotted for the Pd_4 (FIG. **4**B), Cu_4Pd (FIG. **5**B), and the Cu_3Pd (FIG. **6**B).

FIGS. **7**A-**7**C is a schematic depiction of the interaction of reagent and product molecules to atoms comprising the catalyst cluster. FIG. **7**A shows the propane (in a box) adsorbed onto the catalyst. FIG. **7**B shows propylene intermediate adsorbed onto the catalyst. This is a transient condition, with the propylene (showed in a dashed box) converting as it is formed onto the catalyst. FIG. **7**C shows propylene oxide product (in a box) formed on the catalyst. The arrows in the three panels designate the atoms in the cluster to which the substrate propane (FIG. **7**A) and the product propylene oxide (FIG. **7**C) dock.

Upon formation, the product propylene oxide desorbs from the catalyst surface and remains in gas phase for harvesting via typical negative pressure or other means.

It is to be understood that the above description is intended to be illustrative, and not restrictive. For example, the above-described embodiments (and/or aspects thereof) may be used in combination with each other. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from its scope. While the dimensions and types of materials described herein are intended to define the parameters of the invention, they are by no means limiting, but are instead exemplary embodiments. Many other embodiments will be apparent to those of skill in the art upon reviewing the above description. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. In the appended claims, the terms "including" and "in which" are used as the plain-English equivalents of the terms "comprising" and "wherein." Moreover, in the following claims, the terms "first," "second," and "third," are used merely as labels, and are not intended to impose numerical requirements on their objects. Further, the limitations of the following claims are not written in means-plus-function format and are not intended to be interpreted based on 35 U.S.C. § 112, sixth paragraph, unless and until such claim limitations expressly use the phrase "means for" followed by a statement of function void of further structure.

As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” “more than” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. In the same manner, all ratios disclosed herein also include all subratios falling within the broader ratio.

One skilled in the art will also readily recognize that where members are grouped together in a common manner, such as in a Markush group, the present invention encompasses not only the entire group listed as a whole, but each member of the group individually and all possible subgroups of the main group. Accordingly, for all purposes, the present invention encompasses not only the main group, but also the main group absent one or more of the group members. The present invention also envisages the explicit exclusion of one or more of any of the group members in the claimed invention.

The embodiment of the invention in which an exclusive property or privilege is claimed is defined as follows:

1. A one pot method for generating propylene oxide, the method comprising:

a) depositing a plurality of catalyst clusters onto a substrate, wherein the deposited clusters comprise no more than 30 atoms of metal and contain no oxide;

b) contacting propane with the catalyst clusters in the presence of oxygen to convert the propane to the propylene oxide.

2. The method as recited in claim **1** wherein the metal is selected from the group consisting of copper, palladium, platinum, silver, gold, cobalt, and combinations thereof.

3. The method as recited in claim **1** wherein the catalysts are rigidly positioned, relative to each other.

4. The method as recited in claim **1** wherein the substrate is a rigid substrate.

5. The method as recited in claim **4** wherein the rigid substrate is a metal oxide selected from the group consisting of aluminum oxide, iron-oxide, silica oxide, zeolites, titanium oxide, zinc oxide, zirconium oxide, tin oxide, magnesium oxide, cerium oxide and combinations thereof.

6. The method as recited in claim **1** wherein substrate is loose aggregate.

7. The method as recited in claim **1** wherein the method is conducted in a closed reaction vessel and the propane and oxygen are entrained in a carrier gas flowing through the vessel.

8. The method as recited in claim **7** wherein the carrier gas is a relatively inert gas selected from the group consisting of nitrogen, argon, helium, and combinations thereof.

9. The method as recited in claim **1** wherein the method is conducted at ambient pressure.

10. The method as recited in claim **1** wherein the method is conducted at pressures ranging from between about 0.01 atm and 20 atm.

11. The method as recited in claim **1** wherein the method is conducted at temperatures between about 25° C. and 400° C.

12. The method as recited in claim **1** wherein the selectivity for propylene oxide is at least 50 percent at reaction temperatures of between about 25° C. and 400° C.

13. The method as recited in claim **1** wherein the catalyst comprises copper and the clusters contain between 1 and 30 atoms.

14. The method as recited in claim **6** wherein the aggregate is fluidized.

15. The method as recited in claim **1** wherein propylene oxide is generated from propane without any intermediate reaction steps.

16. The method as recited in claim **1** wherein propylene oxide is generated from propane without the production of intermediates.

17. The method as recited in claim **4** wherein the rigid substrate is a carbon based support selected from the group consisting of nanocrystalline diamond, graphite, amorphous carbon, graphene, and combinations thereof.

18. The method as recited in claim **1** wherein the clusters further comprise undercoordinated active sites.

19. The method as recited in claim **1** wherein the clusters are deposited as neat metal.

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