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Exhaustive Identification of Feasible Pathways of the Reaction Catalyzed by a Catalyst with Multiactive Sites via a Highly Effective Graph-Theoretic Algorithm: Application to Ethylene Hydrogenation

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ABSTRACT: Hitherto, no attempt has been made to identify exhaustively feasible pathways for any mechanism of a given reaction catalyzed by a catalyst with multiactive sites. Two stoichiometically exact and definitely feasible mechanisms have been proposed to date for the hydrogenation of ethylene to ethane on biactive-site or triactive-site platinum catalysts. One comprises seven elementary reactions, and the other comprises eight elementary reactions; nevertheless, both mechanisms involve competitive as well as noncompetitive adsorption. Any of these mechanisms gives rise to a multitude of feasible catalytic pathways. The present work exhaustively identifies such feasible pathways by resorting to the inordinately efficient graph-theoretic algorithm based on P-graphs (process graphs). The efficacy of this algorithm has been amply demonstrated by successfully deploying it for several catalysts with single-active sites, but has never been deployed for catalysts with multiactive sites as in the current work. The availability of exhaustively identified feasible pathways for both mechanisms renders it possible to stipulate that the hydrogenation of chemisorbed chemisorbed C_2H_5 is the rate-controlling step: This step is contained in either mechanism.

INTRODUCTION

The catalytic hydrogenation of ethylene to ethane on platinum has been extensively studied in view of its industrial practice, as well as theoretical importance. It is the simplest reaction involving carbon−carbon double-bond hydrogenation.[1−8] One of the two stoichiometrically exact and obviously feasible mechanisms proposed in light of the experimental data is composed of seven elementary reactions involving competitive adsorption,[8] and the other is composed of eight elementary reactions involving competitive as well as noncompetitive adsorption;[3] the former stipulates two active sites, and the latter stipulates three active sites on the catalyst. Any feasible catalytic mechanism gives rise to a multitude of feasible catalytic pathways, signifying the routes for the precursors (i.e., reactants) to transit while they are transformed to the final products.[9−13] The current contribution exhaustively identifies, via synthesis, such feasible pathways by resorting to the inordinately efficient graph-theoretic method based on P-graphs (process graphs).[13−17] Knowing the feasible pathways greatly facilitates the derivation of mechanistic rate expressions to be fitted to experimental data for recovering the parameter values.[18]

The catalysts with multiactive sites, i.e., multifunctional or multiactive-phase oriented catalysts, are increasingly being prepared and characterized experimentally. Moreover, various multiactive-site catalysts, especially biactive-site catalysts, are commercially deployed rapidly. For instance, Pt−Re or Pt−Sn supported on alumina has been extensively applied in hydrogenolysis.[19] Nevertheless, the network structures of multiactive-site catalytic pathways are poorly understood: Their combinatorial complexity far exceeds that of uniactive-site catalytic pathways.[4,5] Moreover, it is extremely difficult, if not impossible, to determine experimentally any catalytic pathway, especially when two or more active sites are involved.

The graph-theoretic method based on P-graphs might be the most effective method for exploring the network structures of multiactive-site catalytic pathways in view of its demonstrated effectiveness for exhaustively identifying the numerous uniactive-site catalytic pathways.[17,18,20−24] Nevertheless, the efficacy of this method based on P-graphs has never been unequivocally tested with any multiactive-site catalytic pathways, as demonstrated hitherto.

Algorithmic methods available for catalytic-pathway identification can be classified in three groups: linear algebraic methods, methods based on convex analysis, and graph-theoretic method based on P-graphs.

Any linear algebraic method presumes that a catalytic reaction remains stationary. It generates the complete set of direct pathways only if they are linearly independent.[10] Another deficiency is that it cannot take into account the irreversibility of the elementary reactions. The methods based on convex analysis have primarily been developed for identifying metabolic networks, which is analogous to catalytic-pathway identification.[25] The targets of the methods, "elementary flux modes" and "extreme pathways," are essentially equivalent to the direct pathways.[26,27] The method based on P-graphs is rooted in

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mathematically rigorous graph theory; it deeply explores the structural information, in addition to the stoichiometry and elementary balances. Its search strategy never yields overlapping alternative search routes, i.e., each pathway is generated exactly once, and thus inordinately efficient. Because of its capability to search for structurally different feasible pathways exhaustively, the P-graph method can also yield the feasible combined pathways, which are often more realistic than the direct pathways.

Petri nets have been proposed for analyzing the dynamics of a system,[28] while P-graphs have been proposed for process synthesis under steady-state conditions. In reaction-pathways analysis, Petri nets can provide information on the initiation of dynamics of a single pathway; in contrast, P-graphs and related algorithms can exhaustively generate alternative feasible pathways at an inordinate speed.

METHODOLOGY

The algorithms for implementing the graph-theoretic method based on P-graphs are rooted in two cornerstones.[13,20] One is the unambiguous representation of the networks of pathways by P-graphs, which are directed bipartite graphs. P-graphs are composed of horizontal bars, representing the nodes for elementary-reaction steps; circles, representing the nodes for active species; and directed arcs, linking these two types of nodes.[14−16] The other is the two sets of axioms, including the six axioms of stoichiometrically feasible pathways, each comprising elementary reactions, for any given overall reaction, and the seven axioms of combinatorially feasible networks of elementary reactions.[13,17,20] These axioms emerge from the truths self-evident by definition (e.g., those pertaining to the starting reactants (precursors) or the final products (targets)), as well as from the fundamental laws and principles (e.g., the conservation of elements (mass) or stoichiometric principle of chemical reactions). Any algorithm strictly based on axioms is mathematically rigorous and tends to be computationally efficient.

Figure 1 illustrates two typical operating units. Note that one type of nodes with circles as their symbols is of the M-type,

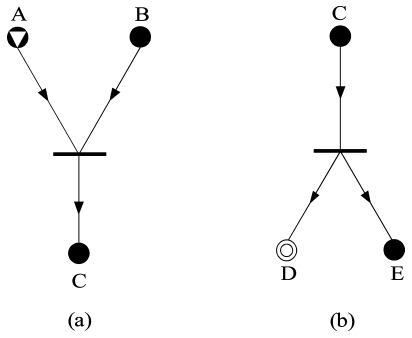

Figure 1. P-graphs of some operating units and their concomitant material streams: (a) Materials A, B, and C, and operating unit ({A, B}, {C}) and (b) Materials C, D, and E, and operating unit ({C}, {D, E}).

representing materials, and the other with horizontal bars as their symbols is of the O-type, representing operating units themselves. An arc, with an arrow indicating the direction of flow of a material stream, is either from a vertex signifying a material to that signifying an operating unit or vice versa. For convenience, the three classes of circles are defined as the symbols for the M-type vertices; see Figure 2. In the context of

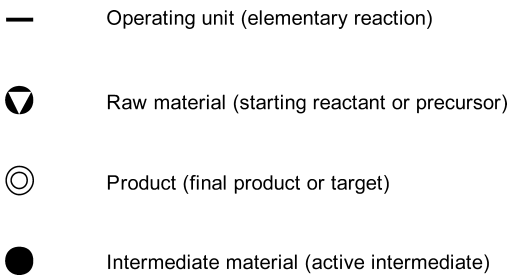

Figure 2. Symbols for P-graphs.

synthesizing the network of a catalytic pathway for its identification, each elementary reaction corresponds to the operating unit (i.e., functioning unit); each starting reactant (precursor), the raw material; each final product, the product; and each active intermediate, the intermediate material.

Axioms. In the light of the reversibility of all the reactions and the stoichiometric exactness of all the reaction steps, the pathway leading from the starting reactants (precursors) through a series of the steps of elementary reactions to the final products (targets) of the overall reaction can be traced backward through every step. Thus, it suffices to determine the pathway only in one direction. Naturally, the complete mechanism is recovered trivially by supplementing the opposite step to each step of the pathway. Moreover, the principle of microscopic reversibility prohibits the inclusion of any cycle in a pathway.[10] These first principles and conditions give rise to the following set of six axioms of feasible reaction pathways for any given overall reaction:

(R1) Every final product (target) is totally produced by the reaction steps represented in the pathway.
(R2) Every starting reactant (precursor) is totally consumed by the reaction steps represented in the pathway.
(R3) Every active intermediate produced by any reaction step represented in the pathway is totally consumed by one or more reaction steps in the pathway, and every active intermediate consumed by any reaction step represented in the pathway is totally produced by one or more reaction steps in the pathway.
(R4) All reaction steps represented in the pathway are defined a priori.
(R5) The network representing the pathway is acyclic.
(R6) At least one elementary-reaction step represented in the pathway activates a starting reactant (precursor).

Since every elementary reaction is reversible, it is comprised of both forward and reverse steps. As a result, at most, either the forward or reverse step of any elementary reaction can be in a pathway to circumvent the formation of a cycle or cycles within it. The directions of the forward and reverse steps of a given elementary reaction are opposite to each other. Hence, they can be simply indicated by the opposite arrows, → and ←, respectively.

To focus on the combinatorial properties of the network comprising the feasible reaction pathways, the condition imposed by Axiom R5 is relaxed except for the cycles formed by the forward and reverse steps of individual elementary reactions. The condition imposed by Axiom R6 is totally relaxed: this axiom does not have any direct bearing on the generation of combinatorially feasible networks. Thus, Axioms R1−R5 can be recast as the seven axioms of the combinatorially feasible reaction networks, leading from the starting reactants (precursors) to

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the final products (targets) of any given overall reaction; this set of axioms is given in the following:

(T1) Every final product (target) is represented in the network.
(T2) Every starting reactant (precursor) is represented in the network.
(T3) Each reaction step represented in the network is defined a priori.
(T4) Every active species represented in the network has at least one path leading to a final product (target) of the overall reaction.
(T5) Every chemical or active species represented in the network must be a reactant for or a product from at least one reaction step represented in the network.
(T6) A reactant of any elementary reaction represented in the reaction network is a starting reactant (precursor), if it is not produced by any reaction step represented in the network.
(T7) The network includes at most either the forward or reverse step of each elementary reaction represented in the network.

Naturally, the last axiom (i.e., Axiom T7) is a consequence of Axiom R5: The two steps of an elementary reaction automatically form a cycle, thereby violating the latter axiom; the inclusion of only one of them is needed to generate a valid pathway from the starting reactants (precursors) to the final products (targets). Nevertheless, Axiom R5 is disregarded for other cyclic loops, exclusion of which may prematurely eliminate combinatorially feasible networks in the algorithmic implementation of the axioms.

Algorithms. The two cornerstones of the method give rise to three highly effective algorithms for synthesizing a stoichiometrically feasible pathway comprising elementary reactions.[13] These three algorithms are: algorithm RPIMSG (maximal structure generation for reaction pathway identification), algorithm RPISSG (solution-structure generation for reaction-pathway identification), and algorithm PBT (pathway-back-tracking for feasible pathway generation).

To minimize the computational difficulty encountered in synthesizing feasible networks of elementary reactions, the mathematical formulation for it should be of minimum complexity. In the framework of the current approach, this is accomplished by generating the maximal structure of the reaction network of interest via algorithm RPIMSG. The maximal structure contains all combinatorially feasible structures, i.e., reaction networks or pathways, each leading from the starting reactants (precursors) to the final products (targets), without violating Axioms T1−T7. Algorithm RPIMSG systematically places all the candidate reaction steps and examines their feasibility in the light of Axioms T1−T7; algorithm RPIMSG represents a slight but judicious adaptation of algorithm MSG originally conceived for the synthesis of a network for the transformation of material species.[16] For the convenience of executing algorithm RPIMSG, the initial network structure is constructed by linking all common nodes representing the chemical or active species in the form of solid circles; the nodes for elementary reactions are in the form of horizontal bars. Moreover, the direction of any arc linking a pair of these two different nodes, one succeeding the other, is not indicated in the initial structure: Every elementary reaction is bidirectional, and, at this juncture, no decision can be made as to which step of this elementary reaction, forward or reverse, should be included in the network. Algorithm RPIMSG consists of two major parts, reduction and composition. In the former, the chemical species i.e., starting reactants (precursors), final products (targets), or active species, i.e., intermediates, and the reaction steps that must not belong to the maximal structure are excluded from the initial structure to the maximum extent possible on the basis of Axioms T1−T7. To initiate the latter, every step of each elementary reaction, which has survived the elimination and is deemed plausible for inclusion, is properly identified on the basis of Axiom T3, and each final product (target) is correctly specified on the basis of Axiom T1. Hereafter, the maximal structure is constructed stepwisely by collecting the reaction steps so as to satisfy Axioms T4 and T5.

Algorithm RPISSG for the solution structure generation yields the set of all combinatorially feasible reaction networks from the maximal structure of reaction networks. This algorithm is generated through the adaptation of algorithm SSG[16] developed for process-network synthesis. Such adaptation has been executed by prudently rewriting the algorithm in the parlance of the graph-theoretic description of the reaction-pathway identification based on the P-graphs mentioned earlier[16,17] and in the light of the axioms of the combinatorially feasible reaction networks (i.e., Axioms T1−T7).

To drastically reduce the computational time necessary to ascertain if each combinatorially feasible reaction network or pathway is indeed a feasible pathway in the light of Axioms R1−R5, a branch-and-bound-like algorithm termed algorithm PBT has been developed. The procedure for implementing algorithm PBT, or equivalently the search through the tree, is initiated at the maximal structure of reaction networks obtained by virtue of algorithm RPIMSG; this structure is at the root of the tree. Algorithm PBT eventually generates the complete set of feasible pathways directly from the maximal structure without necessitating algorithm RPISSG for a given reaction-pathway-identification problem. Algorithm PBT involves three types of steps, i.e., synthetic, retrosynthetic, and back-tracking steps. The synthetic steps that determine the consumption of chemical or active species and the retrosynthetic steps that determine the production of chemical or active species alternate until they result either in a feasible solution or in an infeasible subproblem. The back-tracking steps are invoked if the subproblem examined is infeasible. Algorithm PBT is capable of generating directly all acyclic feasible pathways from the maximal structure.

The procedure for implementing the mathematically rigorous and highly effective methodology outlined herein has been described in detail.[13] Moreover, the software for deploying the algorithms is available at http://www.p-graph.com/demo/rpi/comp_biol_chem/rpi.html.

The methodology has been successfully deployed for exhaustive identifying with inordinate efficiency and speed catalytic and metabolic pathways for catalyzed chemical[17,18,20−24] and biochemical[25,29] reactions, respectively. However, this inordinate efficiency of the methodology has not been validated to date with any catalytic reaction having multiple active sites such as that treated in the current contribution.

RESULTS AND DISCUSSION

Table 1 summarizes the elementary reactions of ethylene hydrogenation proposed by Davis and Davis.[8] It is based on the competitive and noncompetitive adsorption of ethylene and dihydrogen: Some active sites (l_2) are accessible by dihydrogen but not by ethylene, because of the difference in

Table 1. Bi-active-Site Mechanism of Ethylene Hydrogenation Proposed by Davis and Davis[8]

	elementary reactions	E_{for} (kJ/mol)	E_{rev} (kJ/mol)
s_{11}	$H_2 + 2l_1 \leftrightarrow 2Hl_1$	0	25.1
s_{12}	$H_2 + 2l_2 \leftrightarrow 2Hl_2$	0	25.1
s_{13}	$C_2H_4 + 2l_1 \leftrightarrow l_1C_2H_4l_1$	0	37.6
s_{14}	$l_1C_2H_4l_1 + Hl_1 \leftrightarrow C_2H_5l_1 + 2l_1$	39.4	44.8
s_{15}	$l_1C_2H_4l_1 + Hl_2 \leftrightarrow C_2H_5l_1 + l_1 + l_2$	39.4	44.8
s_{16}	$C_2H_5l_1 + Hl_1 \leftrightarrow C_2H_6 + 2l_1$	37.6	112
s_{17}	$C_2H_5l_1 + Hl_2 \leftrightarrow C_2H_6 + l_1 + l_2$	37.6	112

their molecule size. It is similar to the mechanism proposed by Rekoske and co-workers (see Table 2).[3] One difference

Table 2. Tri-active-Site Mechanism of Ethylene Hydrogenation Proposed by Rekoske et al.[3]

	elementary reactions	E_{for} (kJ/mol)	E_{rev} (kJ/mol)
s_{21}	$H_2 + 2l_1 \leftrightarrow 2Hl_1$	0	25.1
s_{22}	$Hl_1 + l_2 \leftrightarrow Hl_2 + l_1$	44.4	41.8
s_{23}	$C_2H_4 + 2l_1 \leftrightarrow l_1C_2H_4l_1$	0	37.6
s_{24}	$l_1C_2H_4l_1 + Hl_2 \leftrightarrow l_1C_2H_5l_1 + l_2$	39.4	44.8
s_{25}	$l_1C_2H_5l_1 + Hl_2 \leftrightarrow C_2H_6 + 2l_1 + l_2$	37.6	112
s_{26}	$H_2 + 2l_3 \leftrightarrow 2Hl_3$	0	25.1
s_{27}	$Hl_3 + l_2 \leftrightarrow Hl_2 + l_3$	44.4	41.8
s_{28}	$2Hl_2 \leftrightarrow H_2 + 2l_2$	25.1	0

between these two mechanisms is that the latter involves hydrogen activation steps (s_{22} and s_{27}), thus leading to a triactive-site mechanism instead of a biactive-site mechanism of the former. To constitute the overall reaction of ethylene hydrogenation on the basis of the triactive-site mechanism, the eighth elementary reaction (s_{28}) is incorporated therein (see Table 2). It is noteworthy that such a multiactive-site mechanism is reported for ethane dehydrogenation, which is the reverse reaction of ethylene hydrogenation.[30]

Tables 1 and 2 also present the forward and reverse activation energies of each elementary step. Reconciling experimental and predicted steady-state kinetics based on the microkinetic model has given rise to these activation energies.[3] Elementary reactions s_{11}, s_{12}, and s_{13} are identical to elementary reactions s_{21}, s_{26}, and s_{23}, respectively; hence, their activation energies should be the same. Elementary reactions s_{14} and s_{15}, as well as elementary reaction s_{24}, involve the hydrogenation of chemisorbed C_2H_4; thus, it would be logical to presume that their activation energies are the same. Similarly, it would be logical to presume that the activation energies of elementary reactions s_{16} and s_{17}, both of which involve the hydrogenation of chemisorbed C_2H_5, are the same.

Tables 3 and 4 list the independent pathways (IP_is) of ethylene hydrogenation resulting from the biactive-site and triactive-site mechanisms, respectively; these pathways have been recovered via the aforementioned graph-theoretic method, based on P-graphs. Note that all of them contain the step for $C_2H_5l_i$ hydrogenation, s_{16}, s_{17}, or s_{25} (37.6 kJ/mol),[3,8] which is deemed to be the rate-determining step: The activation energy of this step is the nearest to that of the overall reaction (37 kJ/mol).[31]

From the probabilistic point of view, it is more logical to represent all the elementary reactions of mechanisms in Tables 1 and 2 as bimolecular reactions.[18] Nevertheless, both

Table 3. Stoichiometrically Feasible Independent Pathways of Ethylene Hydrogenation Based on the Bi-Active-Site Mechanism[8]

designation (IP_i)	pathway
IP_{11}	$s_{11} + s_{13} + 2s_{14} - s_{15} + s_{17}$
IP_{12}	$s_{11} + s_{13} + s_{15} + 2s_{16} - s_{17}$
IP_{13}	$s_{11} + s_{13} + s_{14} + s_{16}$
IP_{14}	$s_{12} + s_{13} - s_{14} + 2s_{15} + s_{16}$
IP_{15}	$s_{12} + s_{13} + s_{14} - s_{16} + 2s_{17}$
IP_{16}	$s_{12} + s_{13} + s_{15} + s_{17}$
IP_{17}	$s_{11} + s_{12} + 2s_{13} + 2s_{14} + 2s_{17}$
IP_{18}	$s_{11} + s_{12} + 2s_{13} + 2s_{15} + 2s_{16}$

Table 4. Stoichiometrically Feasible Independent Pathways of Ethylene Hydrogenation Based on the Tri-Active-Site Mechanism[3]

designation (IP_i)	pathway
IP_{21}	$s_{21} + 2s_{22} + s_{23} + s_{24} + s_{25}$
IP_{22}	$s_{23} + s_{24} + s_{25} + s_{26} + 2s_{27}$
IP_{23}	$s_{23} + s_{24} + s_{25} - s_{28}$

bimolecular and trimolecular representations of elementary reactions give rise to identical results.

Figure 3 is given for the sake of illustration. It contains the P-graph representations of feasible independent pathway IP_{13},

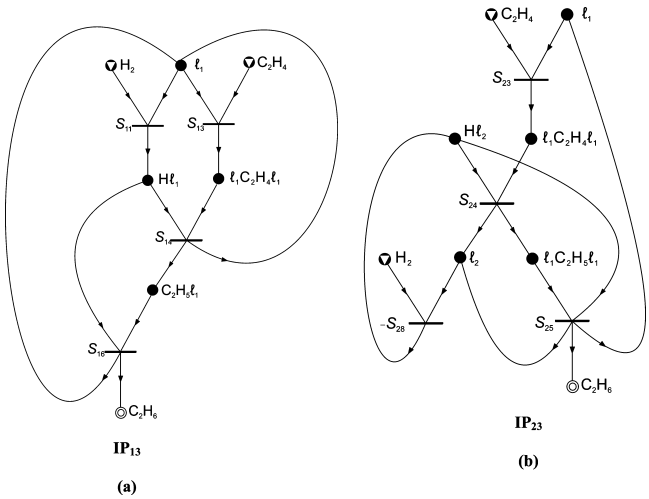

Figure 3. P-graph representations of feasible independent pathways based on: (a) the biactive-site mechanism, IP_{13}, and (b) the triactive-site mechanism, IP_{23}.

based on the biactive-site mechanism, as well as feasible independent pathway IP_{23}, based on the triactive-site mechanism.

CONCLUDING REMARKS

Feasible independent catalytic pathways have been exhaustively identified for the first time by resorting to the inordinately effective graph-theoretic algorithmic method based on P-graphs for two proposed multiactive-site mechanisms for catalytic hydrogenation of ethylene. One is the biactive-site mechanism; and the other, the triactive-site mechanism. Either set of the feasible independent catalytic pathways identified is complete without any redundancy: The P-graphs have been mathematically rigorously defined, and the algorithmic method based on P-graphs is mathematically exacting.

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It is worth noting that all the feasible independent catalytic pathways identified contain an apparently rate-determining step, i.e., hydrogenation of the chemisorbed C_2H_5 radical.[8] This implies that the design of multiactive-site catalysts should focus on the inclusion of such a step.

The computing time required for identifying each set of pathways was roughly 0.02 s on a modestly sized personal computer (PC) (Intel Celeron CPU; E1500@2.20 GHz; 1.99 GB RAM). This computing time is consistent with the computing times spent in identifying all the feasible catalytic as well as metabolic pathways by us. Such inordinate computing efficacy of our methodology is attributable to the fact that the overwhelming majority, almost always far exceeding 90% of combinatorially infeasible pathways, is eliminated at the outset through the construction of the maximal structure, which is a superstructure with minimum complexity, with algorithm RPIMSG. This algorithm is a polynomial algorithm whose complexity increases polynomially as n^2, where n is the number of elementary reactions involved in the proposed mechanism. In diametric contrast, the linear algorithmic methods or the methods based on complex analysis must take into account all the elementary reactions and the networks composed of these elementary reactions from the outset of computing, and thus the complexity of any of these methods and the corresponding computing time accordingly grows exponentially as a function of the number of elementary reactions involved (n).

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