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Synthesis of Startable Reaction Pathways

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Systematically exploring candidate reaction pathways of chemical and biochemical reactions has both theoretical and practical importance. For example, on the basis of the understanding of the mechanism of a complex reaction, its yield may be improved. For this reason many works cover issues on the synthesis of reaction pathways for a given reaction. One of the most effective approach is based on P-graph algorithm capable of generating all possible reaction pathways from the starting reactants (precursors) to final products (targets). This method produces the possible topological structures of the reaction based on dynamic equilibrium state, steady-state circumstances. It is, therefore, crucial to know whether these states can be reached from the initial state of the system, i.e., whether the reaction pathway is structurally startable. A novel algorithm is given in the present work that examines the reaction pathways in terms of structural startability. The algorithm has been demonstrated by applying hydrogenation of ethylene to ethane on biactive-site platinum catalysts. The reduction of the number of potential pathways to be examined during the selection of the best reaction mechanism contributes to the efficiency of reaction engineering.

1. Introduction

A chemical reaction is often composed of a set of individual sub-steps, the elementary reactions. The network representing the connections of the elementary reactions of the overall reaction is traditionally called as reaction pathway, it is the basis for the reaction mechanism. The properties of different pathways (e.g., energy requirements, yield, and geometrical structure of the product) are usually different that make important to determine the best pathway for industrial applications.

There are experimental tools for establishing the reaction mechanism, e.g., recognition of the appearance of reaction intermediates. On the basis of the available intermediates, the set of hypothetical elementary reactions can be determined. There are graph-theoretic methods determining all reaction pathways that can combinatorially be synthesized from the elementary reactions (Fan et al., 2002). These methods are capable of generating all potentially interesting pathways, however, some of these pathways can be infeasible in practice. Though laboratory tests can exclude the infeasible pathways, these tests are usually expensive and time consuming. It is naturally better to reduce the set of potential pathways to the set of feasible pathways as close as it is possible. For example, a pathway is infeasible in practice, if the related reaction cannot be started. Figure 1 shows an example for nonstartable reaction pathway. It is a structurally possible pathway for hydrogenation of ethylene to ethane (Davis and Davis, 2003). Even though each elementary reaction in this pathway is known to be feasible (Fan et al., 2012), the pathway cannot generate ethane without additional external provision. Both elementary reactions S_{12} and S_{13} are executable since all of their inputs are available. Nevertheless, elementary reaction S_{14} cannot be executed since one of its inputs ($H\ell 1$) is not available. Therefore, the overall reaction is not executable by itself on the basis of this pathway.

The purpose of this work is to eliminate those pathways from the systematically generated pathways that cannot be started for structural reason. The formerly developed P-graph framework is used as the basis in determining whether a pathway is structurally startable or not. P-graph framework was originally developed for processing network synthesis (Friedler et al., 1992a), it proved to be useful in solving other types of network problems as far as it has been summarized by Klemeš et al. (2010). Varbanov et al. (2017) reviewed current and future applications.

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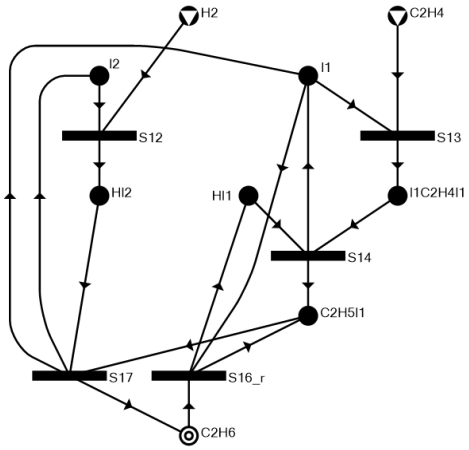


Figure 1: Nonstartable reaction pathway

Approaches for algorithmic generation of reaction-pathways can be based on linear algebra and convex analysis. These approaches determine pathways through a series of basis transformations; however, no effective search strategy is available. Therefore, they are incapable of exhaustively generating the set of feasible pathways for complex reactions. In contrast, graph-theoretic, combinatorial approaches have effective acceleration tools to make complex problems solvable (Lin et al., 2009).
P-graph has been first applied for reaction pathway synthesis by Fan and Friedler (1997) by adopting the P-graph algorithms. Fan et al. (2001) highlighted the specialties of reaction pathway synthesis among process synthesis problems and established new axiomatic system for reaction pathway synthesis of catalytic reactions. Seo et al. (2001) verified the axioms and P-graph algorithms for reaction pathways of metabolic reactions. It has formally been proven that P-graph based reaction pathway synthesis algorithms generate the complete set of direct or structurally minimal pathways identical to those identified by linear algebra and convex analysis based approaches (Barany et al., 2012). Furthermore, P-graph based reaction pathway synthesis algorithm pathway-back-tracking for combinatorially feasible pathway generation is still the only available computer aid to direct generation of the complete set of acyclic combined pathways (Bertok and Fan, 2013). Recent developments resulted in effectively reducing the set of feasible pathways, either modifying the search to generate the minimal pathways (Liu et al., 2015), or taking into account experimental data in addition to stoichiometric information as far as developed by Diaz-Alvaro et al. (2016, 2018) for methanation of carbon dioxide with hydrogen.
The present work extends the P-graph based reaction pathway synthesis algorithms to consider structural startability of a reaction system. The proposed methods have been demonstrated by the well-known hydrogenation of ethylene to ethane on biactive-site platinum catalysts (Davis and Davis, 2003).

2. P-graph approach to reaction pathway synthesis

Stoichiometrically exact candidate pathways or mechanisms of a complex reaction can be determined through the synthesis of networks of plausible steps constituting such mechanisms. Process synthesis frequently arise in industrial applications and are of major interest due to their practical importance and difficulty. P-graph framework provides a series of effective tools to overcome the difficulty coming from the combinatorial nature of process synthesis.

2.1 Reaction pathway synthesis

Reaction pathway synthesis can be defined as a class of process synthesis problems where each species consists of a finite number of chemical elements in a fixed ratio, and these chemical elements are conserved throughout the process. The products of an elementary reaction consist of exactly the same chemical elements as the reactants, and the final products of an overall reaction consist of exactly the same components as the starting reactants.
The combinatorial nature of the problem makes it highly complex. In constituting a mechanism or network directed from the starting reactants towards the final products or vice versa, each elementary reaction contributes the forward, reverse or no step to the network. For example, in a reaction comprising twenty elementary reactions results in $(3^{20}-1) \approx 3.49\ 10^{9}$ possible networks as the search space for selecting the preferred reaction mechanism.

2.2 Combinatorially feasible reaction pathways

Every feasible process has common combinatorial properties that can be exploited in process synthesis (Friedler et al., 1992a). Based on this observation, Friedler et al. (1992b) proposed a method to solve industrial process synthesis problems that drastically reduces the search space. This method has been adapted by Fan et al. (2002) to reaction-pathway synthesis where the elementary reactions and their networks are represented by P-graph. On the P-graph, there are two types of vertices. Elementary reactions are given by vertices shown as horizontal bars while chemical and active species are shown by circles (see Figure 1). If a chemical or active species is a reactant to an elementary reaction, then the vertex representing the species is linked to the vertex representing the elementary reaction by an arc. Similarly, if a chemical or active species is a product from an elementary reaction, then the vertex representing the elementary reaction is linked by an arc to the vertex representing the species.

The reaction pathway leading from the starting reactants to the final products of the overall reaction of interest is combinatorially feasible, if it satisfies the following axioms:

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

These axioms may reduce the search space drastically. For example, the 3^{26}-1 ≈ 2.54 10^{12} search space of 26 elementary reactions of Fischer-Tropsch synthesis (Lin et al., 2009) is reduced to 661 combinatorially feasible pathways. There are algorithms for generating these 661 pathways directly (Fan et al., 2002). Naturally, all feasible pathways is combinatorially feasible, however, a combinatorially feasible pathway is not necessarily feasible. For example, the stoichiometry can be violated by some of the pathways. The next step is to select the stoichiometrically feasible pathways from the set of combinatorially feasible pathways. It can simply be done by examining if the balances of the species are satisfied by all elementary reactions of the reaction pathway and for the overall reaction (Lin et al., 2009). For the Fischer-Tropsch synthesis only 24 pathways are stoichiometrically feasible among the 661 pathways.

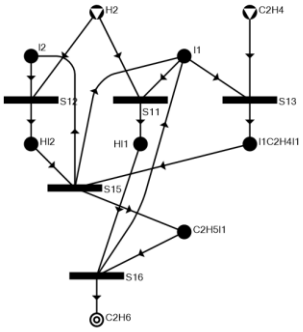
Example

The synthesis of the stoichiometrically feasible reaction pathways are illustrated with the ethylene hydrogenation for the overall reaction $C_2H_4 + H_2 = C_2H_6$. The elementary reactions of the example (Davis and Davis, 2003) are listed in Table 1.

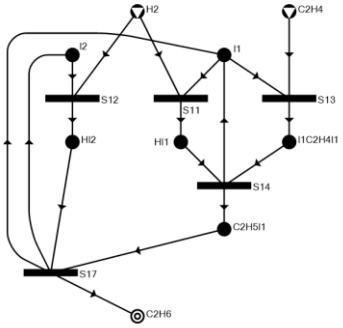
Table 1: Elementary reactions of ethylene hydrogenation

	elementary reaction
S_{11}	$H_2 + 2\,\ell_1 \leftrightarrow 2\,H\ell_1$
S_{12}	$H_2 + 2\,\ell_2 \leftrightarrow 2\,H\ell_2$
S_{13}	$C_2H_4 + 2\,\ell_1 \leftrightarrow \ell_1C_2H_4\ell_1$
S_{14}	$\ell_1C_2H_4\ell_1 + H\ell_1 \leftrightarrow C_2H_5\ell_1 + 2\,\ell_1$
S_{15}	$\ell_1C_2H_4\ell_1 + H\ell_2 \leftrightarrow C_2H_5\ell_1 + \ell_1 + \ell_2$
S_{16}	$C_2H_5\ell_1 + H\ell_1 \leftrightarrow C_2H_6 + 2\,\ell_1$
S_{17}	$C_2H_5\ell_1 + H\ell_2 \leftrightarrow C_2H_6 + \ell_1 + \ell l_2$

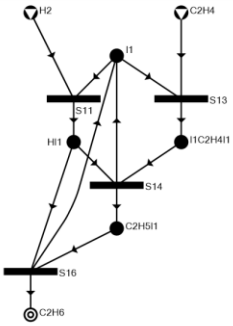
There are 57 combinatorially feasible reaction pathways, eight of them are stoichiometrically feasible as far as it is given by Fan et al. (2012). Figure 2 shows these pathways. The reaction pathway synthesis can be done by the publicly available P-graph Studio software (P-graph, 2018).



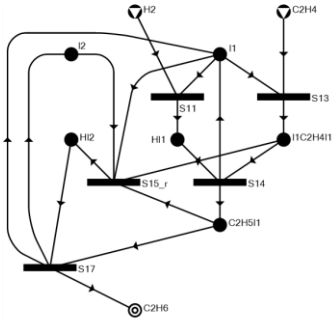
RP_1: $S_{11}+S_{12}+2S_{13}+2S_{15}+2S_{16}$



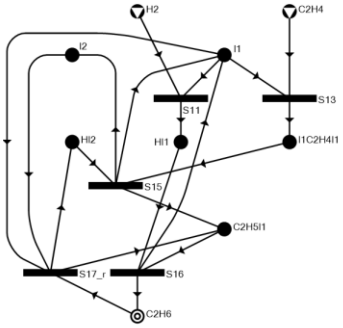
RP_2: $S_{11}+S_{12}+2S_{13}+2S_{14}+2S_{17}$



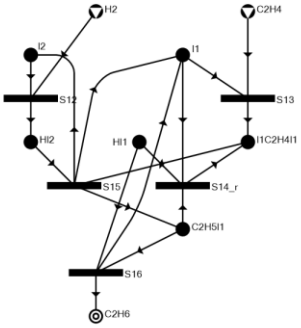
RP_3: $S_{11}+S_{13}+S_{14}+S_{16}$



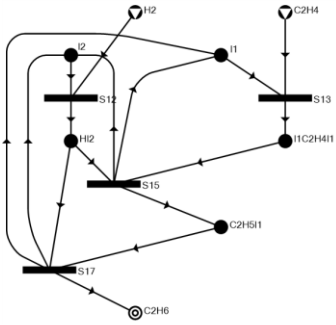
RP_4: $S_{11}+S_{13}+2S_{14}+S_{15}$(reverse)$+S_{17}$



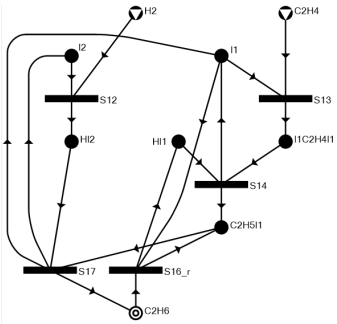
RP_5: $S_{11}+S_{13}+S_{15}+2S_{16}+S_{17}$(reverse)



RP_6: $S_{12}+S_{13}+S_{14}$(reverse)$+2S_{15}+S_{16}$



RP_7: $S_{12}+S_{13}+S_{15}+S_{17}$



RP_8: $S_{12}+S_{13}+S_{14}+S_{16}$(reverse)$+2S_{17}$

Figure 2: Stoichiometrically feasible reaction pathways of ethylene hydrogenation generated by P-graph Studio software

3. Structural startability of a reaction pathway

P-graph algorithms for reaction pathway synthesis serve for exhaustively generating the alternative stoichiometrically feasible reaction pathways. All of these pathways are, however, considered under steady-state conditions. For the determination of the proper mechanisms, it is necessary to investigate whether this steady-state can be achieved from the initial state where only the starting reactants are available. Thus, it is important to recognize if the reaction pathway is startable or not. The relations among the sets of reaction pathways appearing in the paper can be seen in Figure 3.

In the current paper the requirement of structural startability is in focus. Note that, even if several reasons may prevent a reaction pathway to be startable including unfavorable energetic circumstances, in present work, the startability based on structural properties is examined.

The basic statements of the investigation of the structural startability of a reaction pathway are as follows:

- An elementary reaction is structurally startable, if all the chemical or active species consumed by this elementary reaction are available

- A chemical or active species is available, if it is either an initially available species, or it is produced by a structurally startable elementary reaction
- A reaction pathway is structurally startable, if all of its elementary reactions are structurally startable

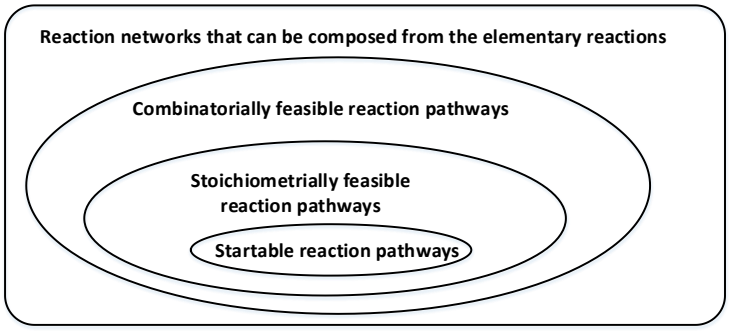


Figure 3: Relations among the sets of reaction pathways during the selection procedure

3.1 P-graph approach for determining the structural startability

The algorithms based on P-graph approach supply all stoichiometrically feasible reaction pathways; each of them contains its elementary reactions together with the set of connected species and the initially available species. A new algorithm is proposed here for examining the structural startability of these pathways. The input of this algorithm is a stoichiometrically feasible reaction pathway in the form of P-graph, together with the set of initially available species, e.g., the starting reactants and the catalysts. The output is the result of the test, whether the reaction pathway is structurally startable or not.
The main steps of the algoritm for determining the structural startability of a stoichiometrically feasible reaction pathway is as follows:

1. Enumeration of the startable elementary reactions (all of their reactants are available)
2. Enumeration of the newly-produced species (the products of the startable elementary reactions that were not available earlier)
3. Extension of the available species with the newly-produced ones
4. If there is no newly-produced species
   if all of the elementary reactions are startable – the reaction pathway is startable
   else – the reaction pathway is nonstartable
   else continue with Step 1

Example revisited

The startability of *RP*5 of Figure 2 is examined. The initially available species are the starting reactants together with the catalysts, i.e., H_2, C_2H_4, ℓ_1, ℓ_2. Table 2 shows the steps of the algorithm resulting nonstartability for *RP*5.

Table 2. Steps of the algorithm for reaction pathway RP_5 of Figure 2

Input:	elementary reactions = {S_{11}, S_{13}, S_{15}, S_{16}, S_{17}(reverse)} chemical and active species = {H_2, C_2H_4, ℓ_1, ℓ_2, $H\ell_1$, $H\ell_2$, $\ell_1C_2H_4\ell_1$, $C_2H_5\ell_1$, C_2H_6} initially available species = {H_2, C_2H_4, ℓ_1, ℓ_2}
Algorithm steps:	1. startable elementary reactions = {S_{11}, S_{13}} 2. newly-produced species = {$H\ell_2$, $\ell_1C_2H_4\ell_1$} 3. available species = {H_2, C_2H_4, ℓ_1, ℓ_2, $H\ell_2$, $\ell_1C_2H_4\ell_1$} 4. newly-produced species $\neq$ { } 1. startable elementary reactions: {S_{11}, S_{13}} 2. newly-produced species = { } 3. available species = {H_2, C_2H_4, ℓ_1, ℓ_2, $H\ell_2$, $\ell_1C_2H_4\ell_1$} 4. newly-produced species = { } not all of the elementary reactions are startable – the reaction pathway is nonstartable

As the result of the algorithm, all pathways shown on Figure 2 are startable pathways excepting RP_5 and RP_8.

4. Conclusions

For industrial processes, it is essential to select the best reaction mechanism of the frequently large number of possible mechanisms. The formerly developed P-graph algorithms are capable of generating all stoichiometrically feasible reaction pathways. Some of these pathways are not necessarily startable. It has been shown that the set of pathways to be considered during the selection of the best pathway can further be reduced by eliminating structurally nonstartable pathways.

Acknowledgments

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