

Graph-theoretic approach to the catalytic-pathway identification of methanol decomposition

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Abstract

Catalytic partial oxidation of methanol (MD) plays a key role in hydrogen production, which is the desirable fuel for both proton exchange membrane and direct methanol fuel cell systems. Thus, the catalytic mechanisms, or pathways, of MD have lately been the focus of intense research interest. Recently, the feasible independent pathways (IP_i's) have been reported on the basis of a set of highly plausible elementary reactions. Nevertheless, no feasible acyclic combined pathways (AP_i's) comprising IP_i's have been reported. Such AP_i's can not be ignored in identifying dominant pathways.

Keywords: methanol decomposition, graph-theory, reaction pathways, independent pathways, acyclic combined pathways

1. Introduction

The graph-theoretic approach resorting to various formal graphs is increasingly being deployed in identifying and representing catalytic or metabolic pathways because of its distinctive efficacy [1-7]. The current contribution represents the latest effort towards such a trend. P-graphs (process graphs) [4, 5, 8-12] have been extensively adopted in exploring the mechanisms of catalytic [7] as well as metabolic reactions [6, 13]. Redundancy can be largely circumvented prior to the follow-up investigation, e.g., the derivation of mechanistic rate equations [7], by determining only the feasible networks of elementary reactions algorithmically and rigorously. It is worth noting that the efficacy of the graph-theoretic method based on P-graphs has been increasing recognized through its wide-ranging applications [14-16].

Fishtik and his collaborators have identified via their reaction-route (RR) graph approach [17-21] the independent pathways for water-gas shift [22, 23] and methanol decomposition (MD) [24]. Nevertheless, revisiting the identical example [23] with our graph-theoretic method based on P-graphs [25] has indicated that their approach or results might not be totally valid. Moreover, the RR graph approach apparently lacks the capability to identify acyclic combined pathways that are no less essential than some of the independent pathways in determining the dominant or ultimate ones, as to be elaborated later.

The current study explores the sets of both independent and acyclic combined pathways of MD by resorting to the graph-theoretic method based on P-graphs. This is followed

by the identification of the dominant, or ultimate, pathway via Kirchhoff's law of current (KLC) or Kirchhoff's law of potential (KPL).

2. Methodology

The graph-theoretic method based on P-graphs is detailed elsewhere [4, 5]. The maximum structure corresponds to the super-structure containing exclusively all combinatorially feasible catalytic pathways, which are solution-structures. Stoichiometrically feasible pathways generated include independent pathways (IP_i 's) and acyclic combined pathways (AP_i 's). Any AP_i is a stoichiometrically feasible combination of IP_i 's, not containing a cycle; therefore, it is highly probable that such a pathway can potentially be dominant under some circumstances. Any pathway containing a cycle, i.e., cyclic pathway, is excluded in view of the principle of microscopic reversibility. A cyclic pathway is formed when two IP_i 's giving rise to the identical overall reaction in opposite directions, and thus, it does not experience any free energy change [5, 26-29].

3. Results and discussion

Table 1 lists 13 available elementary reactions for MD on Pt (1 1 1) [24, 30]. From these elementary reactions, the graph-theoretic method based on P-graphs has yielded stoichiometrically feasible IP_i 's as well as AP_i 's in the current work.

3.1. Independent pathways

Table 2 summarizes the six IP_i 's identified; Figure 1 illustrates P-graphs of IP_2 and IP_3 among them. For clarity, the arcs of IP_2 are drawn in solid line, and those of IP_3 , in dash lines. These six IP_i 's are identical to those reported by Vilekar and his coworkers [24].

Table 2 also contains the overall resistances of the six IP_i 's identified. They have been estimated by resorting to KLC and KLP based on the resistances of individual reaction routes from the literature [24]. Since the overall resistance of IP_3 is the lowest among the six IP_i 's, it can be regarded as the most dominant; this is in accord with what has been reported [24].

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Table 1. Elementary Reactions for Decomposition of Methanol on Pt (1 1 1) [24]

	Elementary reactions
s_1	$\text{CH}_3\text{OH} + \ell \leftrightarrow \text{CH}_3\text{OH}\ell$
s_2	$\text{CH}_3\text{OH}\ell + \ell \leftrightarrow \text{CH}_3\text{O}\ell + \text{H}\ell$
s_3	$\text{CH}_3\text{O}\ell + 2\ell \leftrightarrow \text{CH}_2\text{O}\ell_2 + \text{H}\ell$
s_4	$\text{CH}_2\text{O}\ell_2 \leftrightarrow \text{CHO}\ell + \text{H}\ell$
s_5	$\text{CHO}\ell + \ell \leftrightarrow \text{CO}\ell + \text{H}\ell$
s_6	$\text{CH}_3\text{OH}\ell + \ell \leftrightarrow \text{CH}_2\text{OH}\ell + \text{H}\ell$
s_7	$\text{CH}_2\text{OH}\ell + \ell \leftrightarrow \text{CHOH}\ell + \text{H}\ell$
s_8	$\text{CHOH}\ell + \ell \leftrightarrow \text{COH}\ell + \text{H}\ell$
s_9	$\text{COH}\ell + \ell \leftrightarrow \text{CO}\ell + \text{H}\ell$
s_{10}	$\text{CHOH}\ell + 2\ell \leftrightarrow \text{CO}\ell + 2\text{H}\ell$
s_{11}	$\text{CH}_2\text{OH}\ell + 2\ell \leftrightarrow \text{CH}_2\text{O}\ell_2 + \text{H}\ell$
s_{12}	$\text{CO}\ell \leftrightarrow \text{CO} + \ell$
s_{13}	$2\text{H}\ell \leftrightarrow \text{H}_2 + 2\ell$

Table 2. Feasible Independent Pathways (IP_i's) for Decomposition of Methanol on Pt (1 1 1)

Designation (IP _i)	Pathway	Estimated resistance (Ω)
IP ₁	$s_1 + s_2 + s_3 + s_4 + s_5 + s_{12} + 2s_{13}$	8126.03
IP ₂	$s_1 + s_6 + s_7 + s_8 + s_9 + s_{12} + 2s_{13}$	44.61
IP ₃	$s_1 + s_6 + s_7 + s_{10} + s_{12} + 2s_{13}$	13.71
IP ₄	$s_1 + s_2 + s_3 + s_7 + s_8 + s_9 - s_{11} + s_{12} + 2s_{13}$	15799.53
IP ₅	$s_1 + s_2 + s_3 + s_7 + s_{10} - s_{11} + s_{12} + 2s_{13}$	15768.59
IP ₆	$s_1 + s_4 + s_5 + s_6 + s_{11} + s_{12} + 2s_{13}$	12607.15

3.2. Acyclic combined pathways

Table 3 lists all twenty-seven AP_i's, including the six IP_i's, also identified via our graph-theoretic method [4, 5, 12]. None of the AP_i's in Table 3 has been reported previously. It is worth noting that multiple reaction pathways, i.e., cyclic routes and AP_i's, coexist under the catalytic environment [5, 27, 31]. Naturally, the crucial role that they might play in the reaction should not be totally neglected. Figure 1 also depicts one of the AP_i's, i.e., AP₁₀, comprising the two feasible independent pathways, IP₂ and IP₃. Note that any arcs of IP₂ and IP₃ linked in series overlap, which diverge and subsequently converge at two sets of common nodes for active species, thereby constituting two parallel paths, i.e., routes.

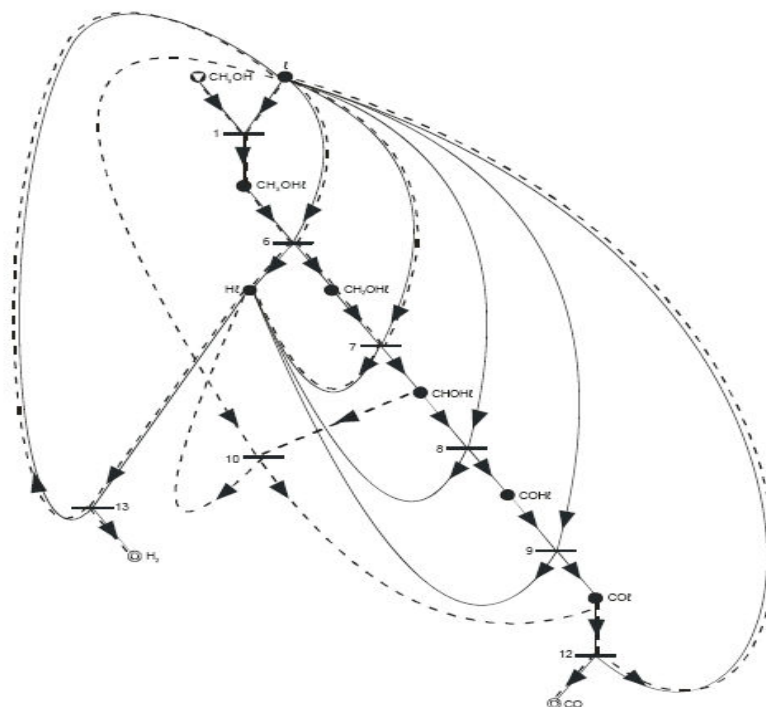


Figure 1. Superimposed P-graph representation of feasible independent pathways IP_2 and IP_3 and acyclic combined pathway AP_{10} , comprising the two independent pathways: The arcs of IP_2 appear as solid lines, and those of IP_3 appear as dashed lines.

The overall resistances of all the AP_i 's, also listed in Table 3, have been computed again by resorting to KLC and KLP (Appendix C). Note that among twenty one AP_i 's, the resistances of AP_{10} (12.93 Ω), AP_{13} (13.70 Ω), AP_{14} (12.92 Ω), AP_{17} (12.62 Ω), AP_{20} (13.69 Ω), AP_{21} (12.91 Ω), AP_{24} (12.93 Ω), AP_{26} (13.69 Ω), and AP_{27} (12.91 Ω) are less than that of IP_3 (13.71 Ω), which has been reported earlier as the dominant pathway [24]. Naturally, it is essential that all the AP_i 's be explored in identifying the dominant pathway; or pathways. Apparently, this can only be accomplished with the current graph-theoretic method based on P-graphs.

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Table 3. Feasible Acyclic Combined Pathways (AP_i's) for Decomposition of Methanol.

AP _i	Pathway	Estimated R. (Ω)
AP ₁	$s_1 + s_2 + s_3 + s_4 + s_5 + s_{12} + 2s_{13}$	8126.03
AP ₂	$s_1 + s_2 + s_3 + s_7 + s_8 + s_9 - s_{11} + s_{12} + 2s_{13}$	15799.53
AP ₃	$s_1 + s_2 + s_3 + s_7 + s_{10} - s_{11} + s_{12} + 2s_{13}$	15768.59
AP ₄	$2s_1 + 2s_2 + 2s_3 + 2s_7 + s_8 + s_9 + s_{10} - 2s_{11} + 2s_{12} + 4s_{13}$	15767.81
AP ₅	$2s_1 + 2s_2 + 2s_3 + s_4 + s_5 + s_7 + s_8 + s_9 - s_{11} + 2s_{12} + 4s_{13}$	18283.49
AP ₆	$2s_1 + 2s_2 + 2s_3 + s_4 + s_5 + s_7 + s_{10} - s_{11} + 2s_{12} + 4s_{13}$	18250.09
AP ₇	$3s_1 + 3s_2 + 3s_3 + s_4 + s_5 + 2s_7 + s_8 + s_9 + s_{10} - 2s_{11} + 3s_{12} + 6s_{13}$	18249.30
AP ₈	$s_1 + s_6 + s_7 + s_8 + s_9 + s_{12} + 2s_{13}$	44.61
AP ₉	$s_1 + s_6 + s_7 + s_{10} + s_{12} + 2s_{13}$	13.71
AP ₁₀	$2s_1 + 2s_6 + 2s_7 + s_8 + s_9 + s_{10} + 2s_{12} + 4s_{13}$	12.93
AP ₁₁	$s_1 + s_4 + s_5 + s_6 + s_{11} + s_{12} + 2s_{13}$	12607.15
AP ₁₂	$2s_1 + s_4 + s_5 + 2s_6 + s_7 + s_8 + s_9 + s_{11} + 2s_{12} + 4s_{13}$	44.54
AP ₁₃	$2s_1 + s_4 + s_5 + 2s_6 + s_7 + s_{10} + s_{11} + 2s_{12} + 4s_{13}$	13.70
AP ₁₄	$3s_1 + s_4 + s_5 + 3s_6 + 2s_7 + s_8 + s_9 + s_{10} + s_{11} + 3s_{12} + 6s_{13}$	12.92
AP ₁₅	$2s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_8 + s_9 + 2s_{12} + 4s_{13}$	44.51
AP ₁₆	$2s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_{10} + 2s_{12} + 4s_{13}$	13.70
AP ₁₇	$3s_1 + s_2 + s_3 + s_4 + s_5 + 2s_6 + 2s_7 + s_8 + s_9 + s_{10} + 3s_{12} + 6s_{13}$	12.62
AP ₁₈	$2s_1 + s_2 + s_3 + 2s_4 + 2s_5 + s_6 + s_{11} + 2s_{12} + 4s_{13}$	2489.15
AP ₁₉	$3s_1 + s_2 + s_3 + 2s_4 + 2s_5 + 2s_6 + s_7 + s_8 + s_9 + s_{11} + 3s_{12} + 6s_{13}$	44.26
AP ₂₀	$3s_1 + s_2 + s_3 + 2s_4 + 2s_5 + 2s_6 + s_7 + s_{10} + s_{11} + 3s_{12} + 6s_{13}$	13.69
AP ₂₁	$4s_1 + s_2 + s_3 + 2s_4 + 2s_5 + 3s_6 + 2s_7 + s_8 + s_9 + s_{10} + s_{11} + 4s_{12} + 8s_{13}$	12.91
AP ₂₂	$2s_1 + s_2 + s_3 + s_6 + 2s_7 + 2s_8 + 2s_9 - s_{11} + 2s_{12} + 4s_{13}$	44.65
AP ₂₃	$2s_1 + s_2 + s_3 + s_6 + 2s_7 + 2s_{10} - s_{11} + 2s_{12} + 4s_{13}$	13.71
AP ₂₄	$3s_1 + s_2 + s_3 + 2s_6 + 3s_7 + 2s_8 + 2s_9 + s_{10} - s_{11} + 3s_{12} + 6s_{13}$	12.93
AP ₂₅	$3s_1 + 2s_2 + 2s_3 + s_4 + s_5 + s_6 + 2s_7 + 2s_8 + 2s_9 - s_{11} + 3s_{12} + 6s_{13}$	44.26
AP ₂₆	$3s_1 + 2s_2 + 2s_3 + s_4 + s_5 + s_6 + 2s_7 + 2s_{10} - s_{11} + 3s_{12} + 6s_{13}$	13.69
AP ₂₇	$3s_1 + 2s_2 + 2s_3 + s_4 + s_5 + s_6 + 2s_7 + s_8 + s_9 + s_{10} - s_{11} + 3s_{12} + 6s_{13}$	12.91

Note: AP₁, AP₂, AP₃, AP₈, AP₉, and AP₁₁ correspond to IP₁, IP₄, IP₅, IP₂, IP₃, and IP₆.

3.3. Computational efficiency

All the IP_i's and AP_i's listed in Tables 2 and 3, respectively, have been generated in less than two seconds on a PC (Intel Pentium 4, CPU 3.06 GHz, and 1 GB RAM), thereby demonstrating that the current method is exceedingly efficient computationally. This has also been demonstrated with catalytic or metabolic reactions substantially more complex than MD [4-7, 12, 13].

4. Concluding remarks

The stoichiometrically feasible independent pathways (IP_i's) and acyclic combined pathways (AP_i's) of methanol decomposition (MD) have been exhaustively identified with the graph-theoretic method based on P-graphs. The potentially dominant pathways of MD have also been identified by resorting to the KLC and KLP as done in a previous work [24]. It has been found that among all the pathways identified, eleven of the twenty one AP_i's can be more dominant than the single IP_i previously reported [24]. These results, therefore, unequivocally imply the importance of identifying AP_i's in addition to IP_i's.

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