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

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ARTICLE INFO

ABSTRACT

Catalytic decomposition of methanol (MD) plays a vital 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 research interest. Recently, the feasible independent pathways (IP_is) have been reported on the basis of a set of highly plausible elementary reactions. Nevertheless, no feasible acyclic combined pathways (AP_is) comprising IP_is have been reported. Such AP_is cannot be ignored in identifying dominant 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 (Djega-Mariadassou & Boudart, 2003; Fan, Bertók, & Friedler, 2002; Fan, Bertók, Friedler, & Shafie, 2001; Lee et al., 2005; Lin, Fan, Shafie, Bertok, & Friedler, 2009; Lin et al., 2008; Murzin, 2007; Murzin, Smeds, & Salmi, 1997). The current contribution represents the latest effort towards such a trend.

The graph-theoretic method based on P-graphs (process graph) (Brendel, Friedler, & Fan, 2000; Fan et al., 2002; Fan et al., 2001; Fan et al., 2005; Friedler, Tarjan, Huang, & Fan, 1992; Friedler, Tarjan, Huang, & Fan, 1993; Friedler, Varga, & Fan, 1995) has been extensively adopted in exploring the mechanisms of catalytic (Fan, Lin et al., 2008; Lin et al., 2009; Lin et al., 2008) as well as metabolic reactions (Lee et al., 2005; Seo et al., 2001). Redundancy can be largely circumvented prior to the follow-up investigation, e.g., the derivation of mechanistic rate equations (Lin et al., 2008), 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 (Fan, Lin et al., 2007;

Fan, Zhang et al., 2007; Fan, Zhang et al., 2008; Halim & Srinivasan, 2002a; Halim & Srinivasan, 2002b; Liu, Fan, Seib, Friedler, & Bertók, 2006; Xu & Diwekar, 2005).

Besides graph-theoretic methods, other methods have been deployed in the identification of catalytic pathways. They are the linear algebraic methods and the method of stoichiometric network analysis.

The linear algebraic-determination of the stoichiometric number for each elementary reaction in a catalytic pathway (mechanism) frequently yields an over-determined system of algebraic equations with the number of constraints exceeding the number of unknowns. This has given rise to the two conventional algorithmic methods for exhaustively identifying the independent feasible catalytic pathways, which can be constituted from a set of plausible elementary reactions. One of the two algorithmic methods is based on combinatorics (Seller, 1971, 1972; Temkin, 1971, 1973). The other algorithmic method is based on mixed integer linear programming (MILP), often via the construction of a super-structure (see, e.g., Hatzimanikatis, Floudas, & Bailey, 1996a; Hatzimanikatis, Floudas, & Bailey, 1996b).

Stoichiometric network analysis (SNA) (Clarke, 1980; Clarke, 1983; Clarke, 1988) is based on qualitative analysis of the nonlinear dynamics reaction pathways. Unlike the linear algebraic methods, SNA refines a pathway of interest in light of constrains (dynamic behavior of chemical reactions, e.g., reactant concentrations). Hence, it can substantially reduce the size of the super-structure of reaction pathways. It is also capable of estimating the potential

stability and instability of the reaction pathways (Ross & Vlad, 1999).

Fishtik and his collaborators have identified via their reaction-route (RR) graph approach (Fishtik, Callaghan, & Datta, 2004a; Fishtik, Callaghan, & Datta, 2004b; Fishtik, Callaghan, & Datta, 2005; Fishtik, Callaghan, & Datta, 2006; Fishtik & Datta, 2001) the independent pathways for water–gas shift (Callaghan et al., 2003; Fishtik & Datta, 2002) and methanol decomposition (MD) (Vilekar, Fishtik, & Datta, 2007). Nevertheless, revisiting the identical example (Callaghan et al., 2003) with our graph-theoretic method based on P-graphs (Fan, Lin et al., 2007) has indicated that their approach or their 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) (Appendix A).

2. Methodology

The graph-theoretic method based on P-graphs is detailed elsewhere (Fan et al., 2002; Fan et al., 2001; Fan et al., 2005); hence, it is only briefly summarized herein: The algorithms to execute the method are rooted in two cornerstones. One is the two sets of axioms, the first of which includes the six axioms of stoichiometrically feasible pathways, each consisting of elementary reactions, for any given overall reaction, and the second of which includes the seven axioms of combinatorially feasible networks of elementary reactions. The other cornerstone is the unambiguous representation of the networks of pathways by P-graphs, which are directed bipartite graphs. P-graphs comprise horizontal bars for the nodes representing elementary-reaction steps, circles for the nodes representing active species, and directed arcs linking these two types of nodes. This graph-theoretic method based on P-graphs has been repeatedly validated to be mathematically rigorous (Friedler et al., 1992; Friedler et al., 1993; Friedler et al., 1995).

The aforementioned axioms and P-graph representation give rise to three highly effective algorithms necessary for synthesizing a stoichiometrically feasible pathway comprising elementary reactions. These algorithms are RPIMSG for maximal-structure generation, RPISSG for solution-structure generation, and PBT for feasible-pathway generation (Fan et al., 2002; Fan et al., 2001; Fan et al., 2005).

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 (Fan et al., 2002; Happel & Sellers, 1983; Happel, Sellers, & Otarod, 1990; Moore, 1972; Sellers, 1984). The algorithms have been successfully deployed to exhaustively identify a number of catalytic and metabolic pathways for catalyzed chemical and biochemical reactions, respectively (Fan et al., 2001; Fan, Lin et al., 2008; Fan et al.,

Table 1
Elementary reactions for decomposition of methanol on Pt (1 1 1) (Vilekar et al., 2007).

	Elementary reactions
s_1	$CH_3OH + * \leftrightarrow CH_3OH^*$
s_2	$CH_3OH^* + * \leftrightarrow CH_3O^* + H^*$
s_3	$CH_3O^* + 2* \leftrightarrow CH_2O^*_2 + H^*$
s_4	$CH_2O^*_2 \leftrightarrow CHO^* + H^*$
s_5	$CHO^* + * \leftrightarrow CO^* + H^*$
s_6	$CH_3OH^* + * \leftrightarrow CH_2OH^* + H^*$
s_7	$CH_2OH^* + * \leftrightarrow CHOH^* + H^*$
s_8	$CHOH^* + * \leftrightarrow COH^* + H^*$
s_9	$COH^* + * \leftrightarrow CO^* + H^*$
s_{10}	$CHOH^* + 2* \leftrightarrow CO^* + 2H^*$
s_{11}	$CH_2OH^* + 2* \leftrightarrow CH_2O^*_2 + H^*$
s_{12}	$CO^* \leftrightarrow CO + *$
s_{13}	$2H^* \leftrightarrow H_2 + 2*$

2005; Lee et al., 2005; Lin et al., 2009; Lin et al., 2008; Seo et al., 2001).

3. Results and discussion

Table 1 lists 13 available elementary reactions for MD on Pt (1 1 1) (Gokhale, Kandoi, Greeley, Mavrikakis, & Dumesic, 2004; Vilekar et al., 2007). 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; Fig. 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 et al. (2007).

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 (Vilekar et al., 2007). 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 (Vilekar et al., 2007).

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 (Fan et al., 2002; Fan et al., 2001). 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 (Happel & Sellers, 1982; Happel & Sellers, 1983). Naturally, the crucial role that they might play in the reaction should not be totally neglected. Fig. 1 also depicts one of the AP$_i$s, i.e., AP$_{10}$, comprising the two feasible independent pathways, IP$_2$ and IP$_3$. Note that any arcs of IP$_2$ and IP$_3$ 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.

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

The overall resistances of all the AP_is, also listed in Table 3, have been computed again by resorting to KLC and KLP (Appendix B). Note that among twenty one AP_is, the resistances of AP_{10} (12.93 Ω), AP_{13} (13.70 Ω), AP_{14} (12.92 Ω), AP_{16} (13.70 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 (Vilekar et al., 2007). Naturally, it is essential that all the AP_is 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.

3.3. Computational efficiency

All the IP_is and AP_is 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 (Fan et al., 2002; Fan et al., 2001; Fan et al., 2005; Lee et al., 2005; Lin et al., 2009; Lin et al., 2008; Seo et al., 2001).

4. Concluding remarks

The stoichiometrically feasible independent pathways (IP_is) and acyclic combined pathways (AP_is) of methanol decomposition 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 (Vilekar et al., 2007). It has been found that among all the pathways identified, ten of the twenty seven AP_is can be more dominant than the single IP_i previous reported (Vilekar et al., 2007). These results, therefore, unequivocally imply the importance of identifying AP_is in addition to IP_is.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.compchemeng.2009.12.004.

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Fig. 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.

Table 3
Feasible acyclic combined pathways (AP_is) for decomposition of methanol on Pt (1 1 1).

AP_i	Pathway	Estimated resistance (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: AP_1, AP_2, AP_3, AP_8, AP_9, and AP_{11} correspond to IP_1, IP_4, IP_5, IP_2, IP_3, and IP_6, respectively.

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