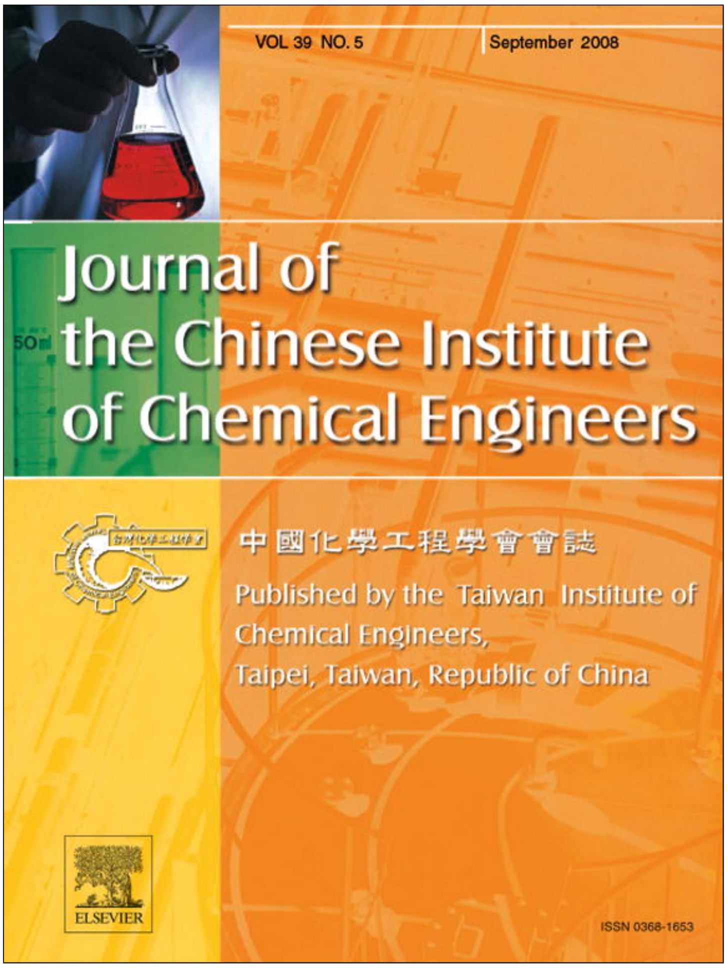
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Graph-theoretic and energetic exploration of catalytic pathways of the water-gas shift reaction

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Abstract

The catalytic mechanisms or pathways of water-gas shift (WGS) reaction have been the focus of intense research interest because of its immense importance in hydrogen production. At the outset, 116 stoichiometrically feasible independent pathways (IP_i's) have been exhaustively generated within 2 s on a PC through a novel graph-theoretic method based on P-graphs (process graphs) from a set of 17 plausible elementary reactions. This is followed by the determination of IP_{18} among these 116 stoichiometrically feasible IP_i's as the plausibly dominant pathway via energetic analysis.

Keywords: Pathway; Water-gas shift; Graph-theoretic; Identification; Catalytic reaction

1. Introduction

The water-gas shift (WGS) reaction, usually carried out catalytically, is ubiquitous in a multitude of technologies ranging from the manufacture of synthetic fuels to hydrogen production (Callaghan *et al.*, 2003; Newsome, 1980); it is one of the most, if not the most, industrially important catalytic reactions of today. It is, therefore, not surprising that much effort has been and is being continually made to investigate this reaction experimentally and/or theoretically (Bunluesin *et al.*, 1998; Fishtik and Datta, 2002; Fu *et al.*, 2001; Shido and Iwasawa, 1992, 1993).

The current contribution focuses on the exhaustive generation of stoichiometrically feasible independent pathways (IP_i's) of the WGS reaction, followed by the identification of energetically favorable feasible pathways. Search for the dominant feasible pathway should be among all the IP_i's. Otherwise, such search would be in vain: It would remain uncertain that the dominant pathway is among them. Moreover, the number of IP_i's generated tends to be vast; nevertheless, only a limited number of them are energetically favorable. Naturally, the identification of the energetically favorable pathways would immensely facilitate the determination of the dominant pathway: It is highly likely that the dominant pathway or pathways are found among them.

At the outset, IP_i's of the WGS reaction have been generated exhaustively by resorting to a novel graph-theoretic method based on P-graphs (process graphs) through the synthesis of all available as well as plausible elementary reactions (Fan *et al.*, 2001, 2002, 2005). This profoundly effective, axiomatic method is the consequence of the mass-conservation law and stoichiometric principle; it has been validated to be mathematically rigorous (Blázsik and Imreh, 1996; Friedler *et al.*, 1992, 1993, 1995).

Subsequently, the energetic diagrams of all the IP_i's have been constructed, each of which comprises the energetic levels of the elementary reactions in the pathway (Callaghan *et al.*, 2003). Any energetically favorable pathway has been explored by its upper energetic and lower energetic boundaries of the diagram. The determination of the dominant pathway can be executed by a variety of means, e.g., regression of the mechanistic rate equations derived from the energetically favorable feasible pathways on the available experimental data (Lin *et al.*, 2008).

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Nomenclature

CSTR	continuous stirred-tank reactor
$\Delta H_{\mathrm{ri}}^{\mathrm{o}}$	enthalpy change of the elementary reaction at the standard state
$\mathrm{IP_i}$	independent pathway
PBT	algorithm for pathway-back-tracking
PFR	plug flow reactor
RPIMSG	algorithm for maximal-structure generation in reaction-pathway identification
RPISSG	algorithm for solution-structure generation in reaction-pathway identification
WGS	water-gas shift

2. Methodology

Presented herein are the method for exhaustively generating the stoichiometrically feasible pathways and the approach for identifying energetically favorable pathways among the resultant $\mathrm{IP_i}$'s.

2.1. Generation of stoichiometrically feasible pathways

The algorithms for implementing the graph-theoretic method based on P-graphs to exhaustively generate $\mathrm{IP_i}$'s are rooted in two cornerstones (Appendix A). One is the two sets of axioms, including the six axioms of each consisting of plausible elementary reactions, for any given overall reaction, and the seven axioms of combinatorially feasible networks of elementary reactions (Fan *et al.*, 2001, 2002, 2005). The other is the unambiguous representation of the networks of pathways by P-graphs, which are directed bipartite graphs. P-graphs comprise horizontal bars, which are the nodes representing an elementary-reaction steps, circles, which are the nodes representing biochemical or active species, and directed arcs linking these two types of nodes (Friedler *et al.*, 1992, 1993, 1995). This graph-theoretic method based on P-graphs has been repeatedly validated to be mathematically rigorous (Blázsik and Imreh, 1996; Friedler *et al.*, 1992, 1993, 1995; Imreh, 2001), and its effectiveness has been increasing recognized through wide-ranging applications (Halim and Srinivasan, 2002a,b; Lee *et al.*, 2005; Lin *et al.*, 2008; Partin, 1998; Seo *et al.*, 2001). Fig. 1 illustrates a P-graph construction of one of the independent pathways, $\mathrm{IP_{73}}$, which has been identified in the current work.

The aforementioned axioms and P-graph representation give rise to three highly effective algorithms necessary for synthesizing an $\mathrm{IP_i}$ comprising elementary reactions. These three algorithms are RPIMSG for maximal-structure generation, RPISSG for solution-structure (combinatorially feasible pathway) generation, and PBT for feasible pathway generation. These algorithms have been deployed to exhaustively identify catalytic and metabolic pathways for catalyzed chemical and biochemical reactions, respectively (Fan *et al.*, 2001, 2002, 2005; Lee *et al.*, 2005; Lin *et al.*, 2008; Seo *et al.*, 2001).

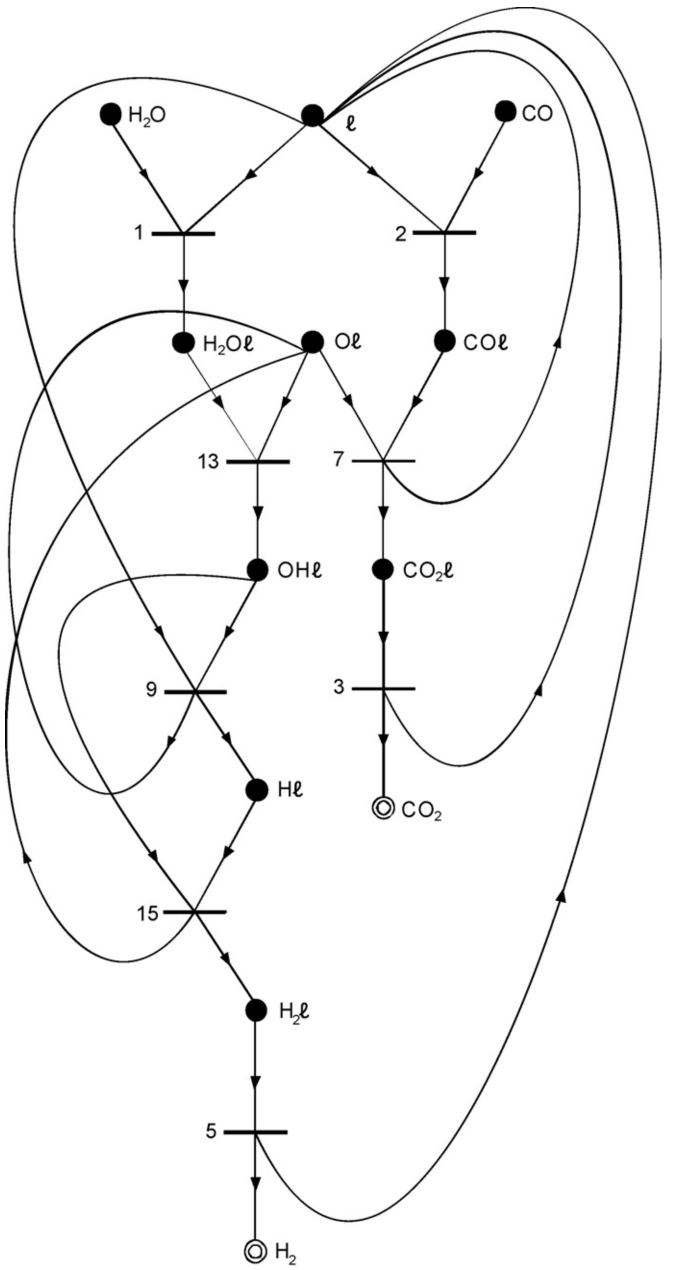

Fig. 1. P-graph representation of independent pathway $\mathrm{IP_{73}}$.

2.2. Identification of energetically favorable pathways

Energetically favorable pathways have been identified by constructing the energetic diagrams of all the $\mathrm{IP_i}$'s generated. The energetic diagram of each pathway is constructed from the standard enthalpy (potential energy) changes of the elementary reactions constituting this pathway. The left boundary of the diagram is defined by the sum of the initiation (adsorption) reactions. Subsequently, the standard enthalpy changes of successively linked elementary reactions are incorporated into the diagram such that the cumulative sum of standard enthalpy changes at each step is as low as possible. The diagram is completed by adding the sum of the termination (desorption) reactions at its right boundary.

3. Results and discussion

Table 1 lists the 17 elementary reactions of a modified microkinetic model for WGS on Cu (1 1 1). The table also lists enthalpy changes of these elementary reactions at the standard state (ΔH°_{ri}'s) (Callaghan *et al.*, 2003). The calculation of these enthalpy changes and the assumptions on which the calculation is based are delineated elsewhere (Callaghan *et al.*, 2003; Fishtik and Datta, 2002; Shustorovich and Sellers, 1998; Waugh, 1999). Table 2 summarizes the IP_i's generated via the graph-theoretic method based on P-graphs from these 17 elementary reactions, which also contains the set of feasible independent pathways obtained in an earlier work (Callaghan *et al.*, 2003). The feasibility of each of the IP_i's in Table 2 has been validated by evaluating its enthalpy change at the standard state by summing those of all the elementary reactions in each pathway. Fig. 1 illustrates one of the feasible pathways, IP_{73}, in terms of the explicit network generated from the graph-theoretic method based on P-graphs. Fig. 2 plots the upper energetic boundary and the lower energetic boundary of the pathways listed in Table 2.

3.1. Stoichiometrically feasible pathways

On the basis of the 17 elementary reactions, which take into account both redox and associate formate mechanisms (Bunluesin *et al.*, 1998; Fu *et al.*, 2001; Shido and Iwasawa, 1992, 1993), the current graph-theoretic method has yielded 116 IP_i's given in Table 2 in less than 2 s on a PC (Intel Pentium 4, CPU 3.06 GHz; and 1 G RAM). Obviously, this set of IP_i's is substantially more comprehensive than those obtained in the earlier work, which number 70 (Callaghan *et al.*, 2003).

The standard enthalpy changes of elementary reactions in each IP_i sum to −11 kcal/mol, which is the standard enthalpy change of the WGS reaction. This provides an additional confirmation concerning the feasibility of each IP_i in Table 2.

Table 1
Elementary reactions for a modified microkinetic model of the catalytic water-gas shift reaction on Cu (1 1 1) (Callaghan *et al.*, 2003)

	Elementary reactions	ΔH°_{ri} (kcal/mol)
s_1	$H_2O + \ell \leftrightarrow H_2O\ell$	−13.6
s_2	$CO + \ell \leftrightarrow CO\ell$	−12.0
s_3	$CO_2\ell \leftrightarrow CO_2 + \ell$	5.3
s_4	$H\ell + H\ell \leftrightarrow H_2\ell + \ell$	2.5
s_5	$H_2\ell \leftrightarrow H_2 + \ell$	5.5
s_6	$H_2O\ell + \ell \leftrightarrow OH\ell + H\ell$	23.8
s_7	$CO\ell + O\ell \leftrightarrow CO_2\ell + \ell$	−17.3
s_8	$CO\ell + OH\ell \leftrightarrow HCOO\ell + \ell$	−20.4
s_9	$OH\ell + \ell \leftrightarrow O\ell + H\ell$	−5.2
s_{10}	$CO\ell + OH\ell \leftrightarrow CO_2\ell + H\ell$	−22.5
s_{11}	$HCOO\ell + \ell \leftrightarrow CO_2\ell + H\ell$	−2.1
s_{12}	$HCOO\ell + O\ell \leftrightarrow CO_2\ell + OH\ell$	3.1
s_{13}	$H_2O\ell + O\ell \leftrightarrow 2OH\ell$	29.0
s_{14}	$H_2O\ell + H\ell \leftrightarrow OH\ell + H_2\ell$	26.3
s_{15}	$OH\ell + H\ell \leftrightarrow O\ell + H_2\ell$	−2.7
s_{16}	$HCOO\ell + OH\ell \leftrightarrow CO_2\ell + H_2O\ell$	−25.9
s_{17}	$HCOO\ell + H\ell \leftrightarrow CO_2\ell + H_2\ell$	0.4

3.2. Energetically favorable pathways

As can be discerned in Fig. 2, at −1.8 kcal/mol, IP_{18}'s upper energetic boundary is the fourth lowest among the 116 stoichiometrically feasible IP_i's, and is higher than those of IP_4, IP_{10}, and IP_{13}. Nevertheless, these 3 IP_i's lower energetic boundaries are exceedingly low. This indicates that the mobility on the catalytic surface of the active species involved are correspondingly low, thereby appreciably diminishing their reactivities. In contrast, at −21.8 kcal/mol, IP_{18}'s lower energetic boundary is the highest, thus indicating that the active species involved in IP_{18} tend to be most mobile on the catalytic surface, which enhances their reactivities. It is, therefore, highly probable that IP_{18} is the dominant pathway. Nevertheless, it is worth noting that the energetic behavior of IP_{19}, IP_{66} and IP_{67} resembles closely that of IP_{18}; hence, they cannot be totally ignored as being potentially dominant pathways.

The current approach for energetic analysis is in stark contrast with the previous study (Callaghan *et al.*, 2003), which identified the three independent pathways, IP_1, IP_3 and IP_{18}, as being the dominant ones by resorting to two heuristics or assumptions: One is that their energetic pathways should fall within a moderate range spanning from 10 to −25 kcal/mol in the energetic diagram, and the other is that the conversions of CO resulting from numerical simulations of the WGS reaction in idealized CSTR and PFR reactors are significantly higher than those of other feasible IP_i's.

It is worth noting that the most plausible dominant pathway, IP_{18}, proceeds according to the redox mechanism, and the pathways, IP_{19}, IP_{66}, and IP_{67}, proceed according to the associate formate mechanism. To discriminate between these two under industrial operating conditions requires further exploration (Rhodes *et al.*, 1995). Nevertheless, the results of the present work appear to be consistent with recent studies on copper-based catalysts (Schumacher *et al.*, 2005; Tabatabaei *et al.*, 2006), thus indicating that the mechanism is redox-prone. Some options are available to promote the redox mechanism. For example, ceria, a material with high oxygen-storage capacity and great stability, may be one of the promising candidates to replace currently by deployed zinc oxide as the support (Bunluesin *et al.*, 1998; Li *et al.*, 2000).

3.3. Combinatorial complexity

The graph-theoretic method based on P-graphs of the current work has yielded a noticeably more comprehensive set of IP_i's (116) than the set obtained in the previous study (70) (Callaghan *et al.*, 2003), which has executed the search by means of a linear algebraic approach (Callaghan *et al.*, 2003; Fishtik and Datta, 2001, 2002): The linear algebraic representation of stoichiometry of the elementary reactions in any pathway gives rise to a exponentially increasing combinatorial complexity (Mavrovouniotis, 1995). This is obvious from the fact that the 17 elementary reactions yield ($3^{17} - 1$), or 129,140,162, possible networks comprising one or more of these elementary reactions.

Table 2
Comparison of the stoichiometrically feasible independent pathways identified in the current work with those identified by Callaghan *et al.* (2003)

Present Work			Callaghan *et al.* (2003)		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mol)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mol)
IP_1	$s_1+s_2+s_3+s_4+s_5+s_6+s_8+s_{11}$	−11	RR_1	$s_1+s_2+s_3+s_4+s_5+s_6+s_8+s_{11}$	−11
IP_2	$s_1+s_2+s_3+s_4+s_5+s_6+s_7+s_9$	−11	RR_2	$s_1+s_2+s_3+s_4+s_5+s_6+s_7+s_9$	−11
IP_3	$s_1+s_2+s_3+s_4+s_5+s_6+s_{10}$	−11	RR_3	$s_1+s_2+s_3+s_4+s_5+s_6+s_{10}$	−11
IP_4	$s_1+s_2+s_3+s_4+s_5+2s_6+s_7-s_{13}$	−11	RR_4	$s_1+s_2+s_3+s_4+s_5+2s_6+s_7-s_{13}$	−11
IP_5	$s_1+s_2+s_3+s_4+s_5+s_{10}+s_{11}-s_{12}+s_{13}$	−11	RR_5	$s_1+s_2+s_3+s_4+s_5+s_{10}+s_{11}-s_{12}+s_{13}$	−11
IP_6	$s_1+s_2+s_3+s_4+s_5+s_9+s_{10}+s_{13}$	−11	RR_6	$s_1+s_2+s_3+s_4+s_5+s_9+s_{10}+s_{13}$	−11
IP_7	$s_1+s_2+s_3+s_4+s_5+s_8+2s_{11}-s_{12}+s_{13}$	−11	RR_7	$s_1+s_2+s_3+s_4+s_5+s_8+2s_{11}-s_{12}+s_{13}$	−11
IP_8	$s_1+s_2+s_3+s_4+s_5-s_8+2s_{10}-s_{12}+s_{13}$	−11	RR_8	$s_1+s_2+s_3+s_4+s_5-s_8+2s_{10}-s_{12}+s_{13}$	−11
IP_9	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+s_{12}+s_{13}$	−11	RR_9	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+s_{12}+s_{13}$	−11
IP_{10}	$s_1+s_2+s_3+s_4+s_5+s_8+s_9+s_{11}+s_{13}$	−11	RR_{10}	$s_1+s_2+s_3+s_4+s_5+s_8+s_9+s_{11}+s_{13}$	−11
IP_{11}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-2s_{12}+s_{13}$	−11	RR_{11}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-2s_{12}+s_{13}$	−11
IP_{12}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_9+s_{13}$	−11	RR_{12}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_9+s_{13}$	−11
IP_{13}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_{10}+s_{13}$	−11	RR_{13}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_{10}+s_{13}$	−11
IP_{14}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_8+2s_{11}+s_{13}$	−11	RR_{14}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_8+2s_{11}+s_{13}$	−11
IP_{15}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_8+s_{12}-s_{13}$	−11	RR_{15}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_8+s_{12}-s_{13}$	−11
IP_{16}	$s_1+s_2+s_3+s_4+s_5+s_6+s_8+s_9+s_{12}$	−11	RR_{16}	$s_1+s_2+s_3+s_4+s_5+s_6+s_8+s_9+s_{12}$	−11
IP_{17}	$s_1+s_2+s_3+s_4+s_5+s_6+s_7+s_{11}-s_{12}$	−11	RR_{17}	$s_1+s_2+s_3+s_4+s_5+s_6+s_7+s_{11}-s_{12}$	−11
IP_{18}	$s_1+s_2+s_3+s_5+s_6+s_7+s_{15}$	−11	RR_{18}	$s_1+s_2+s_3+s_5+s_6+s_7+s_{15}$	−11
IP_{19}	$s_1+s_2+s_3+s_5+s_6+s_8+s_{12}+s_{15}$	−11	RR_{19}	$s_1+s_2+s_3+s_5+s_6+s_8+s_{12}+s_{15}$	−11
IP_{20}	$s_1+s_2+s_3+s_5+s_7+s_9+s_{14}$	−11	RR_{20}	$s_1+s_2+s_3+s_5+s_7+s_9+s_{14}$	−11
IP_{21}	$s_1+s_2+s_3+s_5+s_{10}+s_{14}$	−11	RR_{21}	$s_1+s_2+s_3+s_5+s_{10}+s_{14}$	−11
IP_{22}	$s_1+s_2+s_3+s_5+s_8+s_{11}+s_{14}$	−11	RR_{22}	$s_1+s_2+s_3+s_5+s_8+s_{11}+s_{14}$	−11
IP_{23}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{13}+2s_{14}$	−11	RR_{23}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{13}+2s_{14}$	−11
IP_{24}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{13}+2s_{15}$	−11	RR_{24}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{13}+2s_{15}$	−11
IP_{25}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{14}+s_{15}$	−11	RR_{25}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{14}+s_{15}$	−11
IP_{26}	$s_1+s_2+s_3+s_5+s_7+s_{11}-s_{12}+s_{14}$	−11	RR_{26}	$s_1+s_2+s_3+s_5+s_7+s_{11}-s_{12}+s_{14}$	−11
IP_{27}	$s_1+s_2+s_3+s_5+s_8+s_9+s_{12}+s_{14}$	−11	RR_{27}	$s_1+s_2+s_3+s_5+s_8+s_9+s_{12}+s_{14}$	−11
IP_{28}	$s_1+s_2+s_3+s_5+s_{10}+s_{13}+s_{15}$	−11	RR_{28}	$s_1+s_2+s_3+s_5+s_{10}+s_{13}+s_{15}$	−11
IP_{29}	$s_1+s_2+s_3+s_5+s_8+s_{11}+s_{13}+s_{15}$	−11	RR_{29}	$s_1+s_2+s_3+s_5+s_8+s_{11}+s_{13}+s_{15}$	−11
IP_{30}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}-s_{13}+2s_{14}$	−11	RR_{30}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}-s_{13}+2s_{14}$	−11
IP_{31}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}+s_{14}+s_{15}$	−11	RR_{31}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}+s_{14}+s_{15}$	−11
IP_{32}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}+s_{13}+2s_{15}$	−11	RR_{32}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{12}+s_{13}+2s_{15}$	−11
IP_{33}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_7-s_{12}+s_{16}$	−11	RR_{33}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_7-s_{12}+s_{16}$	−11
IP_{34}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_8+s_{16}$	−11	RR_{34}	$s_1+s_2+s_3+s_4+s_5+2s_6+s_8+s_{16}$	−11
IP_{35}	$s_1+s_2+s_3-s_4+s_5+2s_7-s_8+2s_{15}-s_{16}$	−11	RR_{35}	$s_1+s_2+s_3-s_4+s_5+2s_7-s_8+2s_{15}-s_{16}$	−11
IP_{36}	$s_1+s_2+s_3+s_4+s_5+2s_7-s_8+2s_9-s_{16}$	−11	RR_{36}	$s_1+s_2+s_3+s_4+s_5+2s_7-s_8+2s_9-s_{16}$	−11
IP_{37}	$s_1+s_2+s_3+s_4+s_5+s_{10}+s_{11}-s_{16}$	−11	RR_{37}	$s_1+s_2+s_3+s_4+s_5+s_{10}+s_{11}-s_{16}$	−11
IP_{38}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_{10}+s_{12}-s_{16}$	−11	RR_{38}	$s_1+s_2+s_3+s_4+s_5-s_7+2s_{10}+s_{12}-s_{16}$	−11
IP_{39}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-s_{12}-s_{16}$	−11	RR_{39}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-s_{12}-s_{16}$	−11
IP_{40}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-s_{13}-2s_{16}$	−11	RR_{40}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_{11}-s_{13}-2s_{16}$	−11
IP_{41}	$s_1+s_2+s_3-s_4+s_5+s_7-2s_{12}+s_{13}+2s_{17}$	−11	RR_{41}	$s_1+s_2+s_3-s_4+s_5+s_7-2s_{12}+s_{13}+2s_{17}$	−11
IP_{42}	$s_1+s_2+s_3-s_4+s_5-s_7+2s_8+s_{13}+2s_{17}$	−11	RR_{42}	$s_1+s_2+s_3-s_4+s_5-s_7+2s_8+s_{13}+2s_{17}$	−11
IP_{43}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_9+s_{12}-s_{16}$	−11	RR_{43}	$s_1+s_2+s_3+s_4+s_5+s_7+2s_9+s_{12}-s_{16}$	−11
IP_{44}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}+2s_{14}+s_{16}$	−11	RR_{44}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}+2s_{14}+s_{16}$	−11
IP_{45}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{12}+2s_{15}-s_{16}$	−11	RR_{45}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{12}+2s_{15}-s_{16}$	−11
IP_{46}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}+s_{14}+s_{17}$	−11	RR_{46}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}+s_{14}+s_{17}$	−11
IP_{47}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}-s_{16}+2s_{17}$	−11	RR_{47}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{12}-s_{16}+2s_{17}$	−11
IP_{48}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{13}-2s_{16}+2s_{17}$	−11	RR_{48}	$s_1+s_2+s_3-s_4+s_5+s_7-s_{13}-2s_{16}+2s_{17}$	−11
IP_{49}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{15}-s_{16}+s_{17}$	−11	RR_{49}	$s_1+s_2+s_3-s_4+s_5+s_7+s_{15}-s_{16}+s_{17}$	−11
IP_{50}	$s_1+s_2+s_3+s_4+s_5+s_7+s_9+s_{11}-s_{16}$	−11	RR_{50}	$s_1+s_2+s_3+s_4+s_5+s_7+s_9+s_{11}-s_{16}$	−11
IP_{51}	$s_1+s_2+s_3+s_4+s_5-s_8+2s_{10}-s_{16}$	−11	RR_{51}	$s_1+s_2+s_3+s_4+s_5-s_8+2s_{10}-s_{16}$	−11
IP_{52}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_{11}-s_{16}$	−11	RR_{52}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_{11}-s_{16}$	−11
IP_{53}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{12}+2s_{15}-s_{16}$	−11	RR_{53}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{12}+2s_{15}-s_{16}$	−11
IP_{54}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{13}+2s_{15}+s_{16}$	−11	RR_{54}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{13}+2s_{15}+s_{16}$	−11
IP_{55}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{14}+s_{16}$	−11	RR_{55}	$s_1+s_2+s_3-s_4+s_5+s_8+2s_{14}+s_{16}$	−11
IP_{56}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+2s_{12}-s_{16}$	−11	RR_{56}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+2s_{12}-s_{16}$	−11
IP_{57}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+2s_{13}+s_{16}$	−11	RR_{57}	$s_1+s_2+s_3+s_4+s_5+s_8+2s_9+2s_{13}+s_{16}$	−11
IP_{58}	$s_1+s_2+s_3-s_4+s_5+s_8-s_{12}+s_{13}+2s_{17}$	−11	RR_{58}	$s_1+s_2+s_3-s_4+s_5+s_8-s_{12}+s_{13}+2s_{17}$	−11
IP_{59}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{13}+s_{15}+s_{17}$	−11	RR_{59}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{13}+s_{15}+s_{17}$	−11
IP_{60}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{14}+s_{17}$	−11	RR_{60}	$s_1+s_2+s_3-s_4+s_5+s_8+s_{14}+s_{17}$	−11
IP_{61}	$s_1+s_2+s_3-s_4+s_5+s_8-s_{16}+2s_{17}$	−11	RR_{61}	$s_1+s_2+s_3-s_4+s_5+s_8-s_{16}+2s_{17}$	−11

Table 2 (*Continued*)

Present Work			Callaghan *et al.* (2003)		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mol)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mol)
IP_{62}	$s_1 + s_2 + s_3 + s_4 + s_5 + s_9 + s_{10} + s_{12} - s_{16}$	−11	RR_{62}	$s_1 + s_2 + s_3 + s_4 + s_5 + s_9 + s_{10} + s_{12} - s_{16}$	−11
IP_{63}	$s_1 + s_2 + s_3 + s_5 + s_{10} - s_{12} + s_{13} + s_{17}$	−11	RR_{63}	$s_1 + s_2 + s_3 + s_5 + s_{10} - s_{12} + s_{13} + s_{17}$	−11
IP_{64}	$s_1 + s_2 + s_3 + s_5 + s_{10} + s_{12} + s_{15} - s_{16}$	−11	RR_{64}	$s_1 + s_2 + s_3 + s_5 + s_{10} + s_{12} + s_{15} - s_{16}$	−11
IP_{65}	$s_1 + s_2 + s_3 + s_5 + s_{10} - s_{16} + s_{17}$	−11	RR_{65}	$s_1 + s_2 + s_3 + s_5 + s_{10} - s_{16} + s_{17}$	−11
IP_{66}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 - s_{12} + s_{17}$	−11	RR_{66}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 - s_{12} + s_{17}$	−11
IP_{67}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{17}$	−11	RR_{67}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{17}$	−11
IP_{68}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} + s_{15} - s_{16}$	−11	RR_{68}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} + s_{15} - s_{16}$	−11
IP_{69}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_9 - s_{16} + s_{17}$	−11	RR_{69}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_9 - s_{16} + s_{17}$	−11
IP_{70}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{13} + s_{17}$	−11	RR_{70}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{13} + s_{17}$	−11
IP_{71}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 + s_9 - s_{11} + s_{17}$	−11			
IP_{72}	$s_1 + s_2 + s_3 + s_5 + 2s_6 + s_7 - s_{11} - s_{13} + s_{17}$	−11			
IP_{73}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_9 + s_{13} + s_{15}$	−11			
IP_{74}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{12} + s_{13} + s_{15}$	−11			
IP_{75}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} + s_{13} + 2s_{15} - s_{17}$	−11			
IP_{76}	$s_1 + s_2 + s_3 + s_5 + s_7 + 2s_9 - s_{11} + s_{13} + s_{17}$	−11			
IP_{77}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - 2s_{12} + s_{13} + s_{17}$	−11			
IP_{78}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_9 - s_{12} + s_{13} + s_{17}$	−11			
IP_{79}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{13} + 2s_{14} - s_{17}$	−11			
IP_{80}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} + s_{14} + s_{15} - s_{17}$	−11			
IP_{81}	$s_1 + s_2 + s_3 + s_5 + 2s_7 - s_8 + s_9 + s_{15} - s_{16}$	−11			
IP_{82}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_9 + s_{12} + s_{15} - s_{16}$	−11			
IP_{83}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{13} - 2s_{16} + s_{17}$	−11			
IP_{84}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{12} - s_{16} + s_{17}$	−11			
IP_{85}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 - s_{13} + s_{14}$	−11			
IP_{86}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 - s_{12} + s_{14} + s_{16}$	−11			
IP_{87}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_7 - s_{13} - s_{16} + s_{17}$	−11			
IP_{88}	$s_1 + s_2 + s_3 + s_5 + s_7 + s_{11} - s_{13} + s_{14} - s_{16}$	−11			
IP_{89}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 - s_9 + s_{11} + s_{15}$	−11			
IP_{90}	$s_1 + s_2 + s_3 + s_5 + 2s_6 + s_8 - s_9 + s_{15} + s_{16}$	−11			
IP_{91}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{12} + s_{13} + s_{15}$	−11			
IP_{92}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + 2s_{13} + s_{15} + s_{16}$	−11			
IP_{93}	$s_1 + s_2 + s_3 + s_5 - s_7 + 2s_8 + s_{11} + s_{13} + s_{17}$	−11			
IP_{94}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_{11} - s_{12} + s_{13} + s_{17}$	−11			
IP_{95}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + 2s_{14} - s_{15} + s_{16}$	−11			
IP_{96}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{14} - s_{15} + s_{17}$	−11			
IP_{97}	$s_1 + s_2 + s_3 + s_5 + s_8 - s_9 + 2s_{11} + s_{15} - s_{16}$	−11			
IP_{98}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + 2s_{12} + s_{15} - s_{16}$	−11			
IP_{99}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 - s_{15} - s_{16} + 2s_{17}$	−11			
IP_{100}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_{11} + s_{12} + s_{15} - s_{16}$	−11			
IP_{101}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_{11} - s_{16} + s_{17}$	−11			
IP_{102}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{12} - s_{16} + s_{17}$	−11			
IP_{103}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{13} + s_{15} + s_{16}$	−11			
IP_{104}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{12} - s_{13} + s_{14}$	−11			
IP_{105}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_8 + s_{14} + s_{16}$	−11			
IP_{106}	$s_1 + s_2 + s_3 + s_5 + s_8 + s_9 + s_{13} + s_{14} + s_{16}$	−11			
IP_{107}	$s_1 + s_2 + s_3 + s_5 + s_6 - s_9 + s_{10} + s_{15}$	−11			
IP_{108}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_{10} - s_{11} + s_{12} + s_{15}$	−11			
IP_{109}	$s_1 + s_2 + s_3 + s_5 + s_6 + s_{10} - s_{11} + s_{17}$	−11			
IP_{110}	$s_1 + s_2 + s_3 + s_5 + s_6 - s_9 + s_{10} - s_{12} + s_{17}$	−11			
IP_{111}	$s_1 + s_2 + s_3 + s_5 + s_9 + s_{10} - s_{11} + s_{13} + s_{17}$	−11			
IP_{112}	$s_1 + s_2 + s_3 + s_5 - s_7 + 2s_{10} - s_{11} + s_{13} + s_{17}$	−11			
IP_{113}	$s_1 + s_2 + s_3 + s_5 - s_8 - s_9 + 2s_{10} + s_{15} - s_{16}$	−11			
IP_{114}	$s_1 + s_2 + s_3 + s_5 - s_9 + s_{10} + s_{11} + s_{15} - s_{16}$	−11			
IP_{115}	$s_1 + s_2 + s_3 + s_5 + s_7 - s_8 + s_{10} + s_{15} - s_{16}$	−11			
IP_{116}	$s_1 + s_2 + s_3 + s_5 - s_7 + s_8 + s_{10} + s_{13} + s_{17}$	−11			

To minimize the effort of search, the previous work (Callaghan *et al.*, 2003) has resorted to two heuristics, or assumptions; one is that every elementary reaction is of one of the three types, each with simple stoichiometry (Shustorovich and Sellers, 1998); the other is that the De Donder relations (De Donder and Van Rysselberghe, 1936) are valid in describing the dependency of the rates of elementary reactions on their affinities (Fishtik and Datta, 2001). Invoking these two heuristics, or assumptions, apparently renders it impossible to totally automate the implementation of the linear algebraic

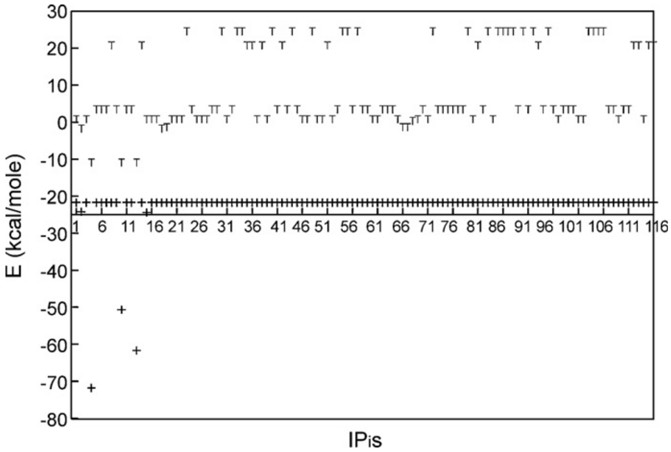

Fig. 2. Upper-energetic (⊤) and lower-energetic (+) boundaries of 116 stoichiometrically feasible pathways identified.

approach for exhaustively identifying the feasible pathways. This is in total contrast to the graph-theoretic method based on P-graphs, which does not invoke any heuristics or assumptions, i.e., it is rigorously axiomatic, thereby enabling it to be executed automatically.

4. Concluding remarks

The stoichiometrically feasible independent pathways (IP_i's) of the catalytic WGS reaction have been exhaustively identified with the graph-theoretic method based on P-graphs. A single potentially dominant or ultimate pathway has emerged from the judicious analysis of energetics of these pathways. The implementation of these two steps is essentially totally axiomatic: Little, if any, heuristic or assumption is involved. Naturally, it entails a multitude of further experimental and theoretical explorations, such as in situ spectroscopic studies (Chen and Chuang, 2003; Weckhuysen, 2002) or reaction energetic analysis (Nakamura *et al.*, 1990), to ascertain if it is indeed the valid pathway, or at least one of the possibly valid pathways, of the catalytic WGS reaction under various conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcice.2008.04.004.

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