Microkinetic Model for the Water Gas Shift Reaction on Supported Copper Catalyst

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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 [1,2]; 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 [2-7].

The current contribution focuses on the exhaustive generation of stoichiometrically feasible 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 stoichiometrically feasible pathways. Otherwise, such search would be in vain: It would remain uncertain that the dominant pathway is among them. Moreover, the number of stoichiometrically feasible pathways generated tends to be vast; nevertheless, only a limited number of them are energetically favorable. Naturally, the identification of the energetically feasible 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, stoichiometrically feasible pathways 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 plausible elementary reactions [8-10]. This profoundly efficient, axiomatic method is the consequence of the mass-conservation law and stoichiometric principle; it has been validated to be mathematically rigorous [11-15].

Subsequently, the energetic diagrams of all the stoichiometrically feasible pathways have been constructed, each of which comprises the energetic levels of the elementary reactions in the pathway [2]. Any energetically feasible 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.

2. Methodology

Present herein are the method for exhaustively generating the stoichiometrically feasible pathways and the approach for identifying energetically feasible pathways among the resultant stoichiometrically feasible pathways.

2.1. Generation of Stoichiometrically Feasible Pathways

The algorithms for implementing the graph-theoretic method based on P-graphs to exhaustively generate stoichiometrically feasible pathways are rooted in two cornerstones. One is the two sets of axioms, including the six axioms of stoichiometrically feasible pathways, each consisting of plausible elementary reactions, for any given overall reaction, and the seven axioms of combinatorially feasible networks of elementary reactions [8-10]. 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 [11-13]. Figure 1 illustrates a P-graph construction of one of the independent pathways, IP_{73}, which have been identified in the current work.

The aforementioned axioms and P-graph representation give rise to three highly efficient algorithms necessary for synthesizing a stoichiometrically feasible pathway 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 [8,9,16-18].

2.2. Identification of Energetically Favorable Feasible Pathways

Energetically favorable feasible pathways have been identified by constructing the energetic diagrams of all the stoichiometrically feasible pathways generated. The energy 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 (111). The table also lists enthalpy changes of these elementary reactions at the standard state (ΔH^{o}_{ri}'s) [2]. Table 2 summarizes the stoichiometrically feasible independent pathways 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 [2]. 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. Figure 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. Figure 2 plots the upper-energetic boundary and the lower-energetic boundary of the pathways listed in Table 2.

Table 1. Modified elementary reaction for the catalytic water-gas shift reaction on Cu (1 1 1) [2]

	Elementary Reactions	ΔH^{o}_{ri} (kcal/mole)
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}	$HCOO\ell + OH\ell \leftrightarrow CO2\ell + H_2O\ell$	-25.9
s_{17}	$HCOO\ell + H\ell \leftrightarrow CO_2\ell + H_2\ell$	0.4

Table 2. Comparison the stoichiometrically feasible independent pathways identified in the current work with those identified by Callaghan et al. [2]

Present Work			Callaghan et al. [2]		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mole)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mole)
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

Table 2. (cont'd.)

Present Work			Callaghan et al. [2]		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mole)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mole)
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

Table 2. (cont'd.)

Present Work			Callaghan et al. [2]		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mole)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mole)
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
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			

Table 2. (cont'd.)

Present Work			Callaghan et al. [2]		
Designation (IP_i)	Mechanism	ΔH^o_{ri} (kcal/mole)	Designation (RR_i)	Mechanism	ΔH^o_{ri} (kcal/mole)
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			

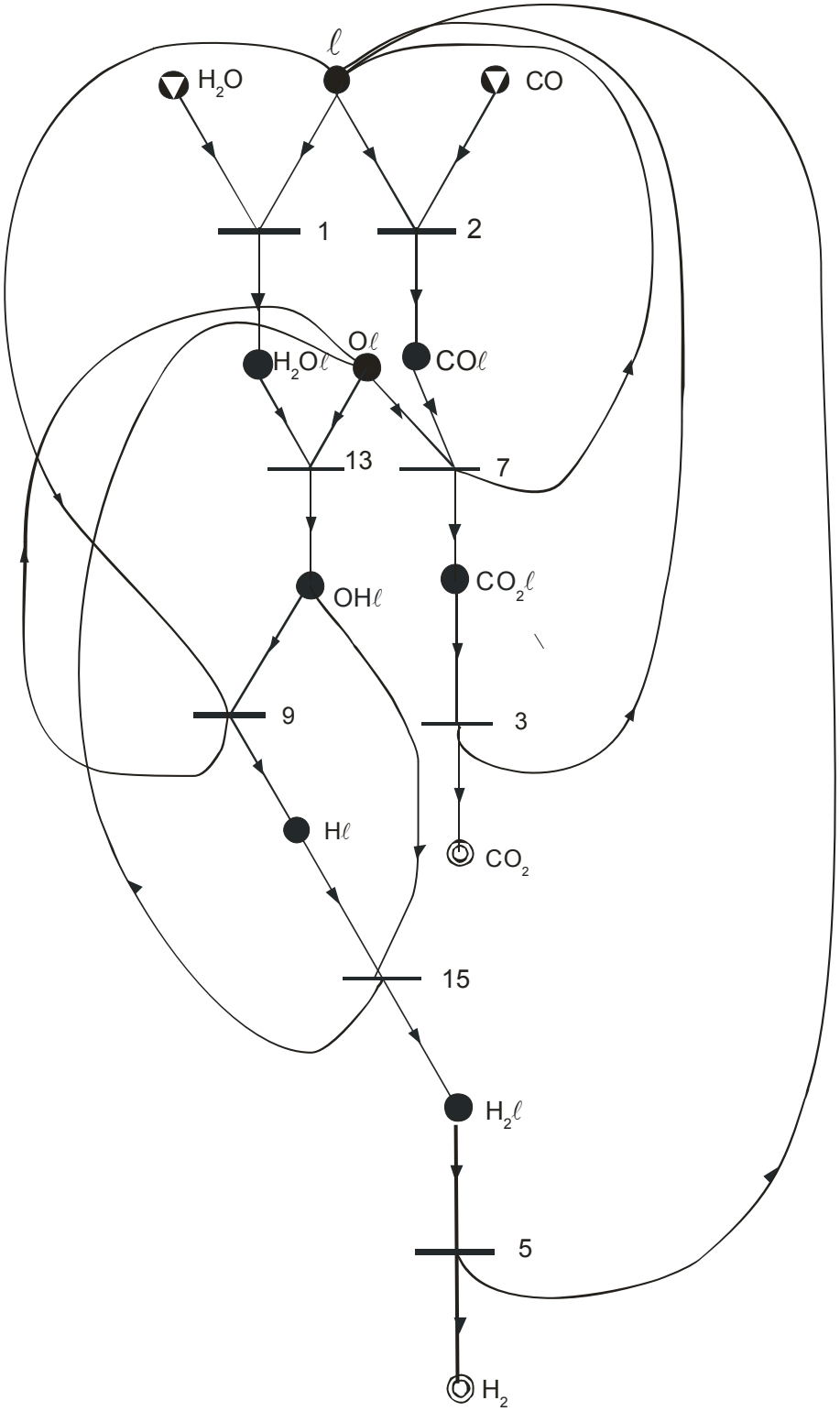

Figure 1. P-graph representation of independent pathway IP_{73}.

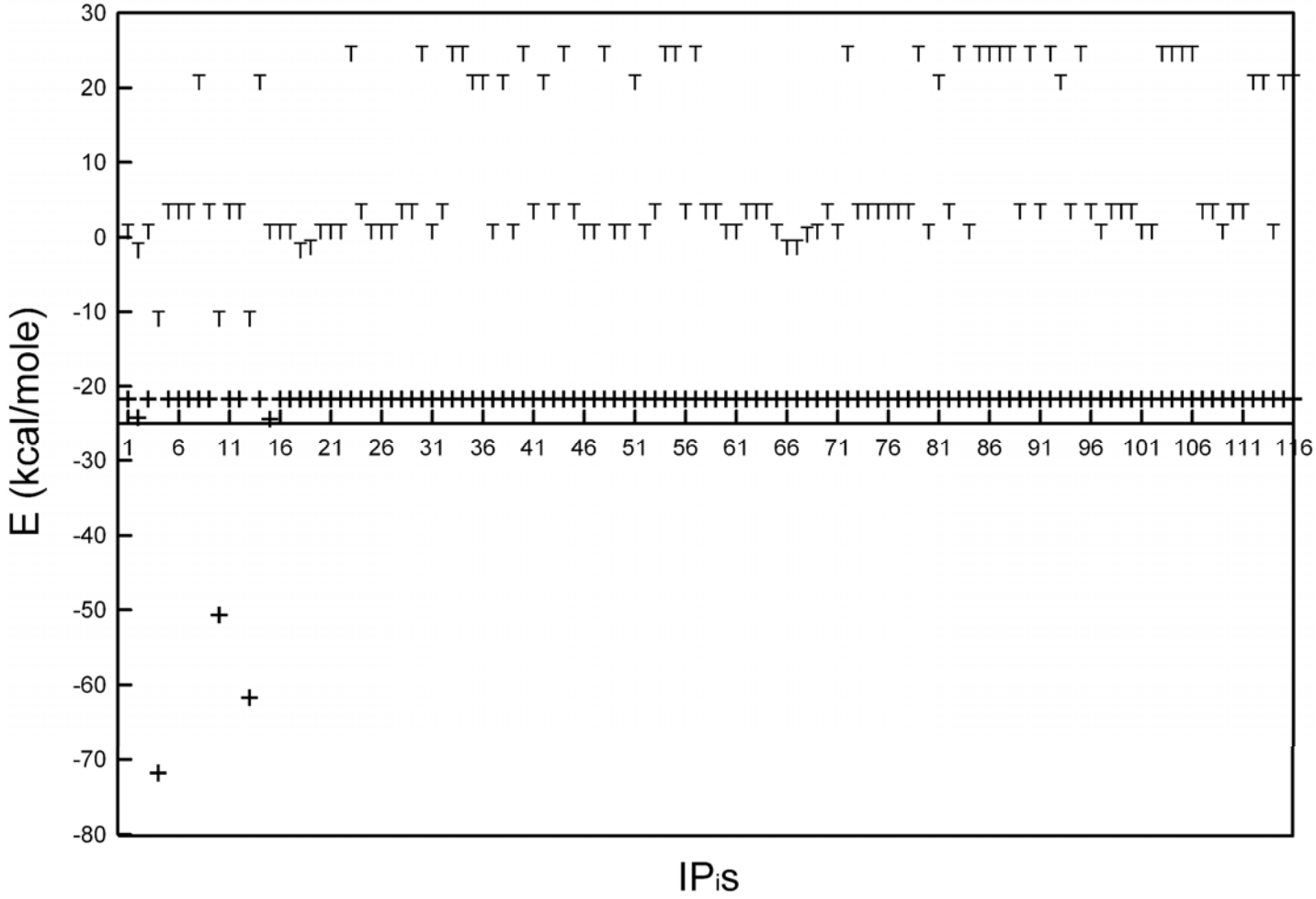

Figure 2. Upper-energetic (┬) and lower-energetic (+) boundaries of 116 stoichiometrically feasible pathways identified.

3.1. Stoichiometrically Feasible Pathways

On the basis of the 17 elementary reactions, which take into account both redox and associate formate mechanisms [3-6], the current graph-theoretic method has yielded 116 stoichiometrically feasible independent pathways (IP_i's) given in Table 2 in less than 2 seconds on a PC (Intel Pentium 4, CPU 3.06GHz; and 1G RAM). Obviously, this set of IP_i's is far more comprehensive than those obtained in the earlier work, which number 70 [2].

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

3.2. Energetically Favorable Pathways

As can be discerned in Figure 2, at -1.8 kcal/mole, 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/mole, IP_{18}'s lower-energetic boundary is 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 can not be totally ignored as being potentially dominant pathways.

The current approach for energetic analysis is in stark contrast with the previous study [2], 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/mole in the energy diagram, and the other is that the conversions of CO resulting from numerical simulations of that WGS reaction in idealized CSTR and PFR reactors are significantly higher than those of other feasible IP_i's.

3.3 Combinatorial Complexity

The graph-theoretic method based on P-graphs of the current work has yielded a substantially more comprehensive set of stoichiometrically feasible pathways (116) than the set obtained in the previous study (70) [2], which has executed the search by means of a linear algebraic approach [2,7,19]: The linear algebraic representation of stoichiometry of the elementary reactions in any pathway gives rise to a exponentially increasing combinatorial complexity [20]. 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.

To minimize the effort of search, the previous work [2] has resorted to two heuristics, or assumptions; one is that every elementary reaction is of one of the three types, each with simple stoichiometry [21]; the other is that the De Donder relations [22] are valid in describing the dependency of the rates of elementary reactions on their affinities [19]. Invoking these two heuristics, or assumptions, apparently renders it impossible to totally automate the implantation of the linear algebraic 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 pathways 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 the resultant stoichiometrically feasible 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 [22,23] or reaction energetic analysis [24], 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.

References

[1] Newsome, D.S. (1980). The water-gas shift reaction. Catal. Rev. - Sci. Eng., 21, 275.

[2] Callaghan, C., Fishtik, I., Datta, R., Carpenter, M., Chmielewski, & M., Lugo, A. (2003). An improved microkinetic model for the water gas shift reaction on copper. Surf. Sci., 541, 21.

[3] Shido, T., & Iwasawa, Y. (1992). Regulation of reaction intermediate by reaction in the water-gas shift reaction on CeO_2, in relation to reactant-promoted mechanism. J. Catal., 136, 493.

[4] Shido, T., & Iwasawa, Y. (1993). Reactant-promoted reaction mechanism for water-gas shift reaction on Rh-doped CeO_2. J. Catal., 141, 71.

[5] Bunluesin, T., Gorte, R.J., & Graham, G.W. (1998). Studies of the water-gas reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties. Appl. Catal. B, 15, 107.

[6] Fu, Q., Weber, A., & Flytzani-Stephanopoulos, M. (2001). Nanostructured Au-CeO_2 catalysts for low-temperature water-gas shift. Catal. Lett., 77, 87.

[7] Fishtik, I., & Datta, R. (2002). A UBI-QEP microkinetic model for the water-gas shift reaction on Cu (1 1 1). Surf. Sci., 512, 229.

[8] Fan, L.T., Bertók, B., & Friedler, F. (1999). Combinatorial framework for the systematic generation of reaction pathways. AIChE Annual Meeting, Dallas, TX.

[9] Fan, L.T., Bertók, B., Friedler, F., & Shafie, S. (2001). Mechanisms of ammonia-synthesis reaction revisited with the aid of a novel graph-theoretic method for determining candidate mechanisms in deriving the rate law of a catalytic reaction. Hung. J. Ind. Chem., 29, 71.

[10] Fan, L.T., Bertók, B., & Friedler, F. (2002). A graph-theoretic method to identify candidate mechanisms for deriving the rate law of a catalytic reaction. Comput. Chem., 26, 265.

[11] Friedler, F., Tarjan, K., Huang, Y.W., & Fan, L.T. (1992). Combinatorial algorithms for process synthesis. Chem. Eng. Sci., 47, 1973.

[12] Friedler, F., Tarjan, K., Huang, Y.W., & Fan, L.T. (1993). Graph-theoretic approach to process synthesis: polynomial algorithm for maximal structure generation. Comput. Chem. Eng., 17, 929.

[13] Friedler, F., Varga, J.B., & Fan, L.T. (1995). Decision-mapping: a tool for consistent and complete decision in process synthesis. Chem. Eng. Sci., 50, 1755.

[14] Blázsik, Z., & Imreh, B. (1996). A note on connection between PNS and set covering problems. Acta Cybernetica, 12, 309.

[15] Imreh, B., Friedler, F., & Fan, L.T. (1996). An algorithm for improving the bounding procedure in solving process network synthesis by a branch-and-bound method, in: Nonconvex Optimization and Its Applications: Developments in Global Optimization, Bomze, I., Csendes, T., Horst, R., Pardalos, P. (Eds.), Kluwer Academic Publishers, Dordrecht, pp.315-348.

[16] Seo, H., Lee, D.Y., Park, S., Fan, L.T., Shafie, S., Bertók, B., & Friedler, F. (2001). Graph-theoretical identification of pathways for biochemical reactions. Biotechnol. Lett., 23, 1551.
[17] Fan, L.T., Shafie, S., Bertók, B., Friedler, F., Lee, D.Y., Seo, H., Park, S., & Lee, S.Y. (2005). Graph-theoretic approach for identifying catalytic or metabolic pathways. J. Chin. Inst. Eng., 28, 1021.
[18] Lee, D.Y., Fan, L.T., Park, S., Lee, S.Y., Shafie, S., Bertók, B., & Friedler, F. (2005). Complementary identification of multiple flux distributions and multiple metabolic pathways. Metab. Eng., 7, 182.
[19] Fishtik, I., & Datta, R. (2001). De Donder relations in mechanistic and kinetic analysis of heterogeneous catalytic reactions. Ind. Eng. Chem. Res., 40, 2416.
[20] Mavrovouniotis, M.L. (1995). Symbolic and quantitative reasoning: design of reaction pathways through recursive satisfaction of constraints. Adv. Chem. Eng., 21, 147.
[21] Shustorovich, E., & Sellers, H. (1998). The UBI-QEP method: a practical theoretical approach to understanding chemistry on transition metal surfaces. Surf. Sci. Rep., 31, 1.
[22] Chen, B., Chuang, S.S.C., (2003). In situ infrared study of oxidative carbonylation of aniline with methanol on Cu-based catalysts. Green Chem., 5, 484.
[23] Weckhuysen, B.M., (2002). Snapshot of a working catalyst: possibilities and limitation of in situ spectroscopy in the field of heterogeneous catalysis. Chem. Comm., 2, 97.
[24] Nakamura, J., Campbell, J.M., & Campbell, C.T., (1990). Kinetics and mechanism of the water-gas shift reaction catalysed by the clean and Cs-promoted Cu (1 1 0) surface: a comparison with Cu (1 1 1). J. Chem. Soc. Faraday Trans., 86, 2725.