

Catalytic Pathways Identification for Partial Oxidation of Methanol on Copper–Zinc Catalysts: $\text{CH}_3\text{OH} + 1/2\text{O}_2 \leftrightarrow \text{CO}_2 + 2\text{H}_2$

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Much effort has been spent to investigate catalytic generation of hydrogen from methanol partial oxidation (MPO) in light of its practical and theoretical importance. Nevertheless, relatively little has been done to gain in-depth understanding of the catalytic mechanisms or pathways of MPO. The exploration of pathways of any catalytic reaction can be greatly facilitated by exhaustively generating at the outset stoichiometrically feasible and independent catalytic mechanisms or pathways (IP_i 's) from a set of plausible elementary reactions by means of our graph-theoretic method based on P-graphs (process graphs). The method is implemented by resorting to the combinatorial algorithms derived from the two sets of rigorously stated axioms on the basis of the mass-conservation law and stoichiometric principle. In the current work, a set of 13 plausible elementary reactions has been proposed for MPO from which six IP_i 's have been generated in less than 1 s with a PC (Pentium 4, CPU 3.06 GHz, and 1 GB RAM). Subsequently, the rate equations of these six IP_i 's have been derived according to the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism. The kinetic constants of the resultant rate equations have been estimated through nonlinear regression of the equations with experimental data. In light of the least-square criterion, IP_2 and IP_6 are deemed potentially dominant pathways.

1. Introduction

Methanol partial oxidation (MPO) yielding hydrogen has been extensively studied in the past decade^{1–3} since hydrogen, by any measure, is an ultraclean fuel. This reaction offers the potential for converting a liquid fuel to hydrogen for use in the portable fuel cell system, which is popularly acknowledged as being a potential candidate to replace the internal combustion engine in vehicles.^{3,4} Among the catalysts for this process, copper–zinc is the most prominent: it is active under moderate conditions (200–300 °C) and generates relatively less CO than other catalysts. It is, therefore, not surprising that much effort has been expended to investigate MPO catalyzed by copper–zinc catalyst experimentally and theoretically.^{2,5,6}

A set of plausible elementary reactions has been proposed by Huang and Chren⁵ for this catalytic reaction. It is mainly based on the mechanism hypothesized by Wachs and Madix.⁷ The latter two have identified methanol molecules chemisorbed on the catalyst's surface, thereby forming methoxide. Subsequently, the methoxide groups interact among themselves as a dual-site reaction, thus generating formaldehyde and chemisorbed hydrogen. Eventually, gas-phase hydrogen is released from the copper–zinc surface by another dual-site reaction among the chemisorbed hydrogen. It remains uncertain if methoxide species is formed as an intermediate on the surface of copper–zinc. Nevertheless, some research groups have confirmed the presence of such an intermediate^{8,9} while others have reported its coexistence with formate species.^{10,11} For simplicity, methoxide is regarded herein as the only intermediate resulting from chemisorbed methanol.

Huang and Chren⁵ have modified this mechanism by assuming the absence of chemisorbed hydrogen on the copper–zinc

Table 1. Elementary Reactions for the Oxidation of Methanol to Produce Hydrogen

	elementary reactions
s_1	$\text{O}_2 + l \leftrightarrow \text{O}_2l$
s_2	$\text{O}_2l + l \leftrightarrow 2\text{O}l$
s_3	$\text{CH}_3\text{OH} + l \leftrightarrow \text{CH}_3\text{OH}l$
s_4	$\text{CH}_3\text{OH}l + \text{O}l \leftrightarrow \text{CH}_3\text{O}l + \text{OH}l$
s_5	$\text{CH}_3\text{OH} + \text{OH}l \leftrightarrow \text{CH}_3\text{O}l + \text{H}_2\text{O}$
s_6	$2\text{CH}_3\text{O}l \leftrightarrow 2\text{CH}_2\text{O}l + \text{H}_2$
s_7	$\text{CH}_2\text{O}l \leftrightarrow \text{CO}l + \text{H}_2$
s_8	$\text{CO}l \leftrightarrow \text{CO} + l$
s_9	$\text{CO} + \text{O}l \leftrightarrow \text{CO}_2 + l$
s_{10}	$\text{H}_2 + \text{O}l \leftrightarrow \text{H}_2\text{O} + l$
s_{11}	$\text{H}_2 + \text{CH}_2\text{O}l \leftrightarrow \text{CH}_3\text{OH} + l$
s_{12}	$\text{CH}_3\text{OH} + \text{O}l \leftrightarrow \text{CH}_2\text{O}l + \text{H}_2\text{O}$
s_{13}	$\text{CH}_2\text{O}l + \text{OH}l \leftrightarrow \text{CH}_3\text{O}l + \text{O}l$

Table 2. Stoichiometrically Feasible Independent Pathways for Oxidation of Methanol to Produce Hydrogen

designation (IP_i)	mechanisms
IP_1	$s_1 + s_2 + 2s_3 + 2s_4 + 2s_6 + 2s_7 + 2s_8 + 2s_9 + 2s_{13}$
IP_2	$s_1 + s_2 + 2s_5 + 2s_7 + 2s_8 + 2s_9 - 2s_{10} - 2s_{13}$
IP_3	$s_1 + s_2 + 2s_7 + 2s_8 + 2s_9 - 2s_{11}$
IP_4	$s_1 + s_2 + 2s_7 + 2s_8 + 2s_9 - 2s_{10} + 2s_{12}$
IP_5	$s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + 2s_7 + 2s_8 + 2s_9 - s_{10}$
IP_6	$s_1 + s_2 + 2s_3 + 2s_4 + 2s_5 + 2s_6 + 2s_7 + 2s_8 + 2s_9 - 2s_{12}$

catalyst due to its low stability at room temperature; this hinders the production of hydrogen from the decomposition of methoxide and chemisorbed formaldehyde groups. Seven elementary reactions are included in this modified mechanism of MPO. If each of these elementary reactions is rewritten as a bimolecular reaction, the number of the elementary reactions in the set increases from 7 to 10. It is worth noting that Huang and Chren⁵ have not asserted that the set of elementary reactions proposed by them constitutes a stoichiometrically feasible mechanism or pathway.

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Table 3. Rate Equations Derived for IP₁, IP₂, IP₅, and IP₆ and the Values of Parameters in the Equations

IP _i 's	Adsorption (ad), surface reaction (sf) and desorption (de) steps. The rate-determining steps are marked with asterisks (*).	Derived rate equations	Fitted parameters
IP ₁	(ad): $O_2 + 2l \xleftarrow{K_{e,1}} 2Ol$ * (sf): $CH_3OH + Ol + l \xleftarrow{K_{sf,1}} CH_3Ol + OHl$ (de): $CH_3Ol + OHl \xleftarrow{K_{de,1}} 2H_2 + CO_2 + l$	$r_1 = \frac{k_{rd,1}O_2}{\left(1 + \frac{H_2CO_2}{K_{sf,1}K_{de,1}CH_3OH} + \frac{2H_2CO_2^{1/2}}{K_{de,1}^{1/2}}\right)^2}$	$k_{rd,1} = 4.6 \cdot 10^5$ $K_{sf,1} = 8.7$ $K_{de,1} = 1.3 \cdot 10^3$ RSS = $1.1 \cdot 10^{-4}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,1}} 2Ol$ (sf): $CH_3OH + Ol + l \xleftarrow{K_{e,1}} CH_3Ol + OHl$ * (de): $CH_3Ol + OHl \xleftarrow{K_{de,1}} 2H_2 + CO_2 + l$	$r_1 = \frac{k_{rd,1}K_{ad,1}O_2^{1/2}}{\left(1 + K_{ad,1}O_2^{1/2} + \frac{2H_2CO_2^{1/2}}{K_{de,1}^{1/2}}\right)^2}$	$k_{rd,1} = 5.9 \cdot 10^{-2}$ $K_{ad,1} = 2.8 \cdot 10^3$ $K_{de,1} = 2.5 \cdot 10^{-14}$ RSS = $7.1 \cdot 10^{-5}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,1}} 2Ol$ (sf): $CH_3OH + Ol + l \xleftarrow{K_{sf,1}} CH_3Ol + OHl$ (de): $CH_3Ol + OHl \xleftarrow{K_{e,1}} 2H_2 + CO_2 + l$ *	$r_1 = \frac{k_{rd,1}K_{ad,1}^{1/2}K_{sf,1}O_2^{1/2}CH_3OH}{\left(1 + K_{ad,1}^{1/2}O_2^{1/2} + 2K_{sf,1}^{1/2}K_{ad,1}^{1/4}O_2^{1/4}CH_3OH^{1/2}\right)^2}$	$k_{rd,1} = 9.5 \cdot 10^4$ $K_{ad,1} = 4.4 \cdot 10^5$ $K_{sf,1} = 8.0 \cdot 10^{-1}$ RSS = $2.4 \cdot 10^{-5}$
IP ₂	(ad): $O_2 + 2l \xleftarrow{K_{e,2}} 2Ol$ * (sf): $CH_3OH + Ol \xleftarrow{K_{sf,2}} CH_2Ol + H_2O$ (de): $2CH_2Ol + H_2O \xleftarrow{K_{de,2}} 2H_2 + CO_2 + l$	$r_2 = \frac{k_{rd,2}O_2}{\left(1 + \frac{H_2CO_2}{K_{de,2}K_{sf,2}CH_3OH} + \frac{H_2CO_2}{K_{de,2}H_2O}\right)^2}$	$k_{rd,2} = 4.6 \cdot 10^5$ $K_{sf,2} = 1.9$ $K_{de,2} = 2.4 \cdot 10^4$ RSS = $1.1 \cdot 10^{-4}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,2}} 2Ol$ (sf): $CH_3OH + Ol \xleftarrow{K_{e,2}} CH_2Ol + H_2O$ * (de): $2CH_2Ol + H_2O \xleftarrow{K_{de,2}} 2H_2 + CO_2 + l$	$r_2 = \frac{k_{rd,2}K_{ad,2}O_2^{1/2}CH_3OH}{\left(1 + K_{ad,2}O_2^{1/2} + \frac{H_2CO_2}{K_{de,2}H_2O}\right)}$	$k_{rd,2} = 6.4 \cdot 10^3$ $K_{ad,2} = 2.0 \cdot 10^5$ $K_{de,2} = 1.0 \cdot 10^{-11}$ RSS = $2.1 \cdot 10^{-5}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,2}} 2Ol$ (sf): $CH_3OH + Ol \xleftarrow{K_{sf,2}} CH_2Ol + H_2O$ (de): $2CH_2Ol + H_2O \xleftarrow{K_{e,2}} 2H_2 + CO_2 + l$ *	$r_2 = \frac{k_{rd,2}K_{ad,2}^{1/2}K_{sf,2}O_2^{1/2}CH_3OH}{1 + K_{ad,2}^{1/2}O_2^{1/2} + \frac{K_{ad,2}^{1/2}K_{sf,2}O_2^{1/2}CH_3OH}{H_2O}}$	$k_{rd,2} = 1.0 \cdot 10^6$ $K_{ad,2} = 4.0$ $K_{sf,2} = 2.7 \cdot 10^4$ RSS = $6.1 \cdot 10^{-5}$
IP ₅	(ad): $O_2 + 2l \xleftarrow{K_{e,5}} 2Ol$ * (sf): $2CH_3OH + Ol + l \xleftarrow{K_{sf,5}} 2CH_3Ol + H_2O$ (de): $2CH_3Ol + 2H_2O \xleftarrow{K_{de,5}} 5H_2 + 2CO_2 + 2l$	$r_5 = \frac{k_{rd,5}O_2}{\left(1 + \frac{H_2CO_2^2}{K_{sf,5}K_{de,5}^2H_2OCH_3OH^2} + \frac{H_2^{5/2}CO_2}{K_{de,5}H_2O}\right)^2}$	$k_{rd,5} = 4.6 \cdot 10^5$ $K_{sf,5} = 9.4 \cdot 10^{-1}$ $K_{de,5} = 4 \cdot 10^1$ RSS = $1.1 \cdot 10^{-4}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,5}} 2Ol$ (sf): $2CH_3OH + Ol + l \xleftarrow{K_{e,5}} 2CH_3Ol + H_2O$ * (de): $2CH_3Ol + 2H_2O \xleftarrow{K_{de,5}} 5H_2 + 2CO_2 + 2l$	$r_5 = \frac{k_{rd,5}K_{ad,5}O_2^{1/2}CH_3OH^2}{\left(1 + K_{ad,5}O_2^{1/2} + \frac{H_2^{5/2}CO_2}{K_{de,5}H_2O}\right)^3}$	$k_{rd,5} = 2.4 \cdot 10^{10}$ $K_{ad,5} = 5.6 \cdot 10^3$ $K_{de,5} = 1.1 \cdot 10^1$ RSS = $2.3 \cdot 10^{-5}$
	(ad): $O_2 + 2l \xleftarrow{K_{ad,5}} 2Ol$ (sf): $2CH_3OH + Ol + l \xleftarrow{K_{sf,5}} 2CH_3Ol + H_2O$ (de): $2CH_3Ol + 2H_2O \xleftarrow{K_{e,5}} 5H_2 + 2CO_2 + 2l$ *	$r_5 = \frac{k_{rd,5}K_{ad,5}^{1/2}K_{sf,5}O_2^{1/2}CH_3OH^2H_2O}{\left(1 + K_{ad,5}^{1/2}O_2^{1/2} + \frac{K_{ad,5}^{1/4}K_{sf,5}^{1/2}O_2^{1/4}CH_3OH}{H_2O^{1/2}}\right)^2}$	$k_{rd,5} = 2.8 \cdot 10^2$ $K_{sf,5} = 3.5 \cdot 10^{10}$ $K_{de,5} = 1.3 \cdot 10^{10}$ RSS = $2.2 \cdot 10^{-4}$

Table 3. (Continued)

IP _i 's	Adsorption (ad), surface reaction (sf) and desorption (de) steps. The rate-determining steps are marked with asterisks (*).	Derived rate equations	Fitted parameters
IP ₆	(ad): $O_2 + 2l \xleftarrow{K_{e,6}} 2Ol$ *	$r_6 = \frac{k_{rd,6}O_2}{\left(1 + \frac{H_2CO_2}{K_{sf,6}K_{de,6}CH_3OH} + \frac{CH_3OH^{1/2}H_2CO_2^{1/2}}{K_{de,6}^{1/2}H_2O^{1/2}}\right)^2}$	$k_{rd,6} = 4.6 \cdot 10^5$ $K_{sf,6} = 5.9$ $K_{de,6} = 6.2 \cdot 10^5$ $RSS = 1.1 \cdot 10^{-4}$
	(sf): $2CH_3OH + Ol + l \xleftarrow{K_{sf,6}} 2CH_3Ol + H_2O$		
	(de): $2CH_3Ol + H_2O \xleftarrow{K_{de,6}} CH_3OH + 2H_2 + CO_2 + 2l$		
IP ₆	(ad): $O_2 + 2l \xleftarrow{K_{ad,6}} 2Ol$	$r_6 = \frac{k_{rd,6}K_{ad,6}O_2^{1/2}CH_3OH^2}{\left(1 + K_{ad,6}O_2^{1/2} + \frac{CH_3OH^{1/2}H_2CO_2^{1/2}}{K_{de,6}H_2O^{1/2}}\right)^2}$	$k_{rd,6} = 1.4 \cdot 10^{10}$ $K_{ad,6} = 1.1 \cdot 10^4$ $K_{de,6} = 3.7 \cdot 10^{-8}$ $RSS = 2.1 \cdot 10^{-5}$
	(sf): $2CH_3OH + Ol + l \xleftarrow{K_{e,6}} 2CH_3Ol + H_2O$ *		
	(de): $2CH_3Ol + H_2O \xleftarrow{K_{de,6}} CH_3OH + 2H_2 + CO_2 + 2l$		
IP ₆	(ad): $O_2 + 2l \xleftarrow{K_{ad,6}} 2Ol$	$r_6 = \frac{k_{rd,6}K_{ad,6}^{1/2}K_{sf,6}O_2^{1/2}CH_3OH^2}{\left(1 + K_{ad,6}^{1/2}O_2^{1/2} + \frac{K_{ad,6}^{1/4}K_{sf,6}^{1/2}O_2^{1/4}CH_3OH}{H_2O^{1/2}}\right)^2}$	$k_{rd,6} = 3.2 \cdot 10^5$ $K_{sf,6} = 8.9 \cdot 10^8$ $K_{de,6} = 1.3 \cdot 10^4$ $RSS = 1.4 \cdot 10^{-4}$
	(sf): $2CH_3OH + Ol + l \xleftarrow{K_{sf,6}} 2CH_3Ol + H_2O$		
	(de): $2CH_3Ol + H_2O \xleftarrow{K_{e,6}} CH_3OH + 2H_2 + CO_2 + 2l$ *		

The production of hydrogen from MPO has been extensively investigated experimentally; in contrast, relatively meager effort has been made to explore its catalytic mechanisms or pathways. The current work aims at the exhaustive generation of stoichiometrically feasible, independent catalytic pathways (IP_i's) of MPO from a set of plausible elementary reactions by means of our graph-theoretic method based on P-graphs (process graph). This is followed by the derivation of a rate equation on the basis of each IP_i according to the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism.^{12,13} The resultant rate equations are fitted to experimental data; the pathway corresponding to the best-fitting rate equation is deemed most likely to be the dominant or ultimate one. This identification of the dominant or ultimate pathway is greatly facilitated by various means, such as the spectroscopic determination of generation of active intermediate involved in the pathways of concern.^{14–16} Obviously, the rate equation based on the dominant pathway would have practical utility in designing and operating industrial processes for implementing MPO.

2. Methodology

2.1. Theoretical. Presented herein are the graph-theoretic method based on P-graphs and the LHHW formalism. The former exhaustively identifies stoichiometrically feasible pathways for a given catalytic reaction, and the latter is for deriving the rate expressions on the basis of the resulting pathways, i.e., mechanisms.

2.1.1. Graph-Theoretic Method Based on P-graphs for Determining the Stoichiometrically Feasible Pathways. The algorithms for implementing our graph-theoretic method based on P-graphs are rooted in two cornerstones (Appendix A). One is the two sets of axioms, including the six axioms of stoichiometrically feasible pathways, each consisting of elementary reactions, for any given overall reaction, and the seven axioms of combinatorially feasible networks of elementary reactions.^{14–16} 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.^{17–19} This graph-theoretic method based on P-graphs has been repeatedly validated to be mathematically rigorous,^{17–22} and its effectiveness has been increasing recognized through wide-ranging applications.^{23–28}

The aforementioned axioms and P-graphs representation give rise to three highly effective algorithms necessary for synthesizing a stoichiometrically feasible pathway comprising elementary reactions. These three algorithms are RPMSG for maximal-structure generation, RPSSG for solution-structure generation, and PBT for feasible-pathway generation. The maximum structure corresponds to the superstructure containing exclusively all combinatorially feasible catalytic pathways, which are solution structures. The algorithms have been successfully deployed to exhaustively identify catalytic and metabolic pathways for catalyzed chemical and biochemical reactions, respectively.^{14,16,24,27}

2.1.2. Derivation of Rate Equations According to the LHHW Formalism. The LHHW formalism offers an effective paradigm for deriving a surface-reaction kinetic model for heterogeneous catalytic reactions.^{29,30} It takes into account all major physicochemical phenomena involved in a heterogeneous catalytic reaction. Such phenomena include adsorption, surface reaction, and desorption. In formulating the model, active sites on the surface of a catalyst are explicitly identified, thereby resulting in an active site balance.³¹

The complexity and computational effort involved in deriving the rate equations according to the LHHW formalism can be minimized by various means. For instance, the stoichiometrically feasible IP_i's, in which the most abundant surface intermediates as identified by spectroscopy do not participate, are eliminated prior to the derivation.

2.2. Experimental. 2.2.1. Catalyst Preparation. The catalyst comprising 40% of Cu supported on ZnO was prepared via the co-precipitation method.^{32,33} The procedure was as follows. At the outset, aqueous solutions of two nitrate salts were prepared, one by dissolving 8.4 g of Cu(NO₃)₂ into 300 mL of deionized water and the other by dissolving 13 g of Zn(NO₃)₂ into the same amount of solvent. The mixture of these two solutions

was fed dropwise into an aqueous solution of Na_2CO_3 prepared by dissolving 10 g of Na_2CO_3 also in 300 mL of deionized water. This mixture was then preheated to 80 °C with continuous stirring for 60 min. The resulting solution was then cooled to room temperature and filtered; the cake retained on the filter was ground and calcinated at 400 °C for 12 h. The calcined cake in the form of powder was pelletized, crushed, and sieved into particles from 40 to 45 mesh.

2.2.2. Measurements of Catalytic Activity. Experiments were performed in a vertical quartz-tube reactor inside a cylindrical furnace. Because of the high exothermicity of MPO, the catalyst bed was formed by blending 0.05 g of the Cu/ZnO catalyst with 0.45 g of SiO_2 (40 to 45 mesh). This bed was sandwiched between plugs of quartz wool. SiO_2 , inert under the experimental conditions, facilitated the dispersion of catalysts within the catalyst bed, thereby preventing the occurrence of hotspots. Prior to each experimental run, the catalyst bed was preheated from room temperature to 250 °C in a 4 °C/min ramp and maintained at 250 °C for an hour, during which a stream containing 30 mol % of H_2 and 70 mol % of N_2 was passed through it. The data were acquired via a gas chromatograph equipped with MolSieve 5A and Hayesep T columns to separate the products. Influences of internal and external mass-transfer resistances were explored prior to the catalytic investigations. The internal resistance was examined by varying the catalysts' particle sizes. Two sizes of the particles were used—one ranged from 20 to 40 mesh, and the other ranged from 40 to 45 mesh. No difference was observed between the particle sizes. The external resistance was probed by changing the weight loading of the catalyst bed. Two loadings were selected—in one of the loadings, 0.03 g of catalyst was mixed with 0.37 g of SiO_2 , and in the other, 0.05 g of catalyst was mixed with 0.45 g of SiO_2 . No difference was observed between the two loadings. The details of measurements, catalyst characterization and catalytic reactivity testing are available elsewhere.^{34,35}

3. Results and Discussion

3.1. Feasible IP_i 's. Table 1 summarizes 13 elementary reactions, including 10 (s_1 through s_{10}) from the original set proposed by Huang and Chren⁵ and 3 (s_{11} through s_{13}) newly proposed by us, which can plausibly constitute the pathways or mechanisms of MPO on ZnO catalyst. From these 13 elementary reactions, the current graph-theoretic approach based on P-graphs has generated six stoichiometrically feasible independent pathways (IP_i 's), which are listed in Table 2, within a second on a PC (Intel Pentium 4, CPU 3.06 GHz; and 1 GB RAM). Note that Table 2 also contains the pathway proposed by Huang and Chren⁵ as one of the IP_i 's (IP_5).

3.2. Rate Equations. Methoxide has been known determined to be the most abundant surface intermediates in MPO on copper's surface.^{7,36} Thus, IP_3 and IP_4 , not involving methoxide, have been eliminated. Table 3 lists the 12 rate equations obtained for the remaining four IP_i 's, including IP_1 , IP_2 , IP_5 , and IP_6 , derived according to the LHHW formalism. Specifically, the assumption that the adsorption, surface reaction, or desorption step is rate-determining in each of the four IP_i 's has given rise to these rate equations (see Appendix B).

3.3. Parameter Estimation. Each of the rate equations for the remaining four IP_i 's, i.e., IP_1 , IP_2 , IP_5 , and IP_6 , contains four parameters. When the adsorption step is rate-determining, they are $k_{\text{rd},i}$, $K_{\text{e},i}$, $K_{\text{sf},i}$, and $K_{\text{de},i}$; the surface reaction step, $k_{\text{rd},i}$, $K_{\text{ad},i}$, $K_{\text{e},i}$, and $K_{\text{de},i}$; the desorption step, $k_{\text{rd},i}$, $K_{\text{ad},i}$, $K_{\text{sf},i}$, and $K_{\text{e},i}$. Three sets of the four parameters include $K_{\text{e},i}$; however, its magnitude is inordinately large for MPO.⁵ Thus, the term with

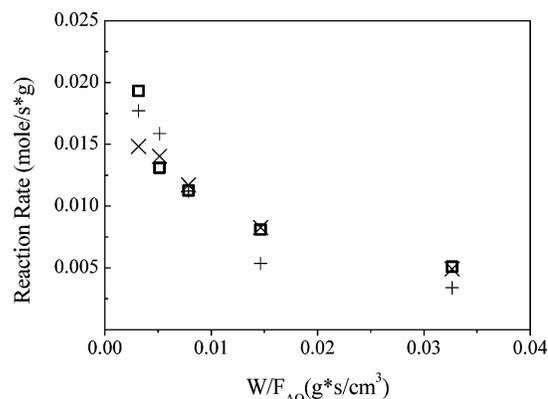


Figure 1. Comparison between the experimentally measured and estimated reaction rates for IP_2 and IP_6 : □, experimental data; ×, estimated values for IP_2 ; and +, estimated values for IP_6 . Note that the confidence intervals at 95% level of the experimental data are not presented to maximize the contrast between the experimentally data and estimated values.

$K_{\text{e},i}$ in the denominator can be regarded as negligibly small, thereby leaving three parameters to be estimated through the nonlinear regression of the four rate equations, listed in Table 3, on the experimental data. Specifically, nonlinear regression has been performed by resorting to an adoptive random search method subject to the criterion of the least residual sum of squares (RSS).^{37,38} Table 3 summarizes the resultant values of the three parameters in the 12 rate equations derived from the four IP_i 's. Among these 12 rate equations, those derived from IP_2 , IP_5 , and IP_6 by assuming that the surface-reaction step is rate-determining and those derived from IP_1 by assuming that the desorption step is rate-determining result in the lowest RSS. Moreover, the computed rates from the equations derived from IP_2 , IP_5 , and IP_6 most closely follow the experimentally measured variational trend of the reaction rate as a function of the contact time. Nevertheless, $K_{\text{de},5}$ in the equation derived on the basis of IP_5 is unusually large for the desorption step at equilibrium state. This, therefore, leaves only IP_2 and IP_6 as the potentially most dominant or ultimate pathways. Figure 1 compares the experimentally measured and estimated reaction rates for IP_2 and IP_6 . To discriminate between these two requires further exploration, such as in-situ spectroscopic studies³⁹ and reaction energetic analysis.⁴⁰

4. Concluding Remarks

The stoichiometrically feasible pathways of MPO have been exhaustively identified in a short time by using the graph-theoretic method based on P-graphs. The rate equations of these pathways have been derived according to the LHHW formalism. Subsequently, the rate constants of these equations have been estimated through the nonlinear regression of the equations on the available experimental data. Two potentially dominant pathways have been determined on the basis of the least-square criterion.

The current work ushers in a comparatively novel paradigm for determining the pathway of a catalytic reaction, initiating the rigorous graph-theoretic and exhaustive identification of stoichiometrically feasible independent pathways at the outset, followed by theoretical, mechanistic, computational, and/or experimental exploration of the reaction on the basis of such pathways.

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search method. This work was supported by Army Research Office under Grant No. DAAD 19-03-1-0100, W911NF-05-1-0194, and Hungarian Scientific Research Fund under Project No. F61227.

Supporting Information Available: Appendix A presents the graph-theoretic method based on P-graphs, and Appendix B presents the derivation of the rate equation for IP₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Nomenclature

IP_{*i*}, independent pathway

$k_{rd,i}$, forward rate constant for the surface reaction step of pathway *i*

$K_{ad,i}$, equilibrium constant for the adsorption step of pathway *i*

$K_{eq,i}$, equilibrium constant for surface reaction step of pathway *i*

$K_{de,i}$, equilibrium constant for the desorption step of pathway *i*

LHHW, Langmuir–Hinshelwood–Hougen–Watson

MPO, methanol partial oxidation

PBT, algorithm for pathway-back-tracking

RPIMSG, algorithm for maximal structure generation in reaction-pathway identification

RPISG, algorithm for solution-structure generation in reaction-pathway identification

RSS, residual sum of squares

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