

# PREDICTIONS OF ACTIVITY PATTERNS FOR METHANE REFORMING BASED ON COMBINATORIAL PATHWAY GENERATION AND ENERGETICS

Raúl E. Valdés-Pérez

Computer Science Department, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Ilie Fishtik

Department of Chemical and Biochemical Engineering, The University of Iowa,  
Iowa City, IA 52242, USA

Andrew V. Zeigarnik

Laboratory of Chemical Kinetics and Catalysis, Lomonosov Academy of Fine Chemical  
Technology, Moscow, 117571 Russia

## ABSTRACT

We have applied the method to carbon formation in CO<sub>2</sub> reforming of methane over eight transition metals, starting with a list of 164 elementary steps and published UBI-QEP calculations of their activation energies and using the MECHEM program for combinatorial pathway generation. The predicted coking pattern Fe > Ni > Ru > Rh, Ir, Pd > Cu, Pt is consistent with experimental results from the literature. Current work focuses on deriving an activity pattern for the production of CO+H<sub>2</sub> in methane reforming.

## INTRODUCTION

During the past decades, physical chemistry and surface science have provided a basis for understanding catalytic processes at the molecular level.<sup>1</sup> However, the search for active, stable, and selective catalysts for any given chemical process still remains largely empirical and is performed in the face of great uncertainty about most aspects of the process.<sup>2</sup> For example, ideally the choice of catalysts should rely on knowledge of the reaction mechanism and kinetics and of the physical properties and structure of the catalyst, promoters, and support, among others. However, usually neither the mechanism nor kinetics of elementary steps is known.

Recent advances in computational methods have enabled searching comprehensively for hypothetical reaction pathways<sup>3</sup> and bulk calculations of activation energies and enthalpies of candidate elementary steps.<sup>4</sup> A combination of these techniques holds the promise of increasing the suite of systematic tools that can guide catalyst design.<sup>5</sup>

This article reports an initial attempt to combine combinatorial pathway generation with energetics for the purpose of catalyst design. The method adopts MECHEM<sup>2,6-8</sup> – a computer aid for mechanism elucidation. To develop the approach, we focused on predicting the relative coking properties of metal single-crystal catalysts for carbon dioxide reforming of methane. This choice is motivated by the availability of published data and by the importance of coking control in the conversion of natural gas to syngas.<sup>9</sup> The method enables finding a list of “best” coking pathway/catalyst pairs, which are then used to construct a qualitative ranking of metals in their activity toward coking. The advantage of basing a predicted activity pattern on the relative barriers of pathways rather than the relative barriers of presumed rate-determining steps is that it removes the need to postulate rate-determining steps, which ultimately only make sense in the context of a larger pathway.

Our starting data, taken entirely from Ref. 4, consist of 164 elementary steps and their activation energies for eight transition-metal catalysts. The single-crystal catalysts were Cu(111), Ni(111), Pd(111), Pt(111), Rh(111), Ru(001), Ir(111), and Fe(110). Activation energies were calculated by the UBI-QEP method.<sup>10</sup> The accuracy of the calculated activation energies was claimed to be about 2 kcal/mol.<sup>4</sup>

## METHODS

*Background on Computational Methods.* MECHEM<sup>2,6-8</sup> is an ongoing, multi-year project whose goals are to provide high level assistance for the elucidation or exploration of chemical reaction mechanisms. Technical details can be found in specialized journals.<sup>11</sup> The basic approach is to comprehensively search the possible elementary reactions and pathways in a “first principles” spirit. The principle involved is that an elementary step involves a small (user-adjustable) number of changes in the bonding of the reactants. Since in mechanism elucidation the reaction starting materials are known, MECHEM builds elementary steps of the form *known reactants* → X + Y and then solves for all possible structures of the unknowns X and Y by using ad-hoc graph algorithms and assuming, say, at most three or four total changes (cleavage or formation) to the connectivity of all the molecular graphs, including X and Y. One could contrast this “logical” approach to generating elementary steps with an alternative empirical approach that, say, only generates steps that follow specific reaction schemata such as migratory insertion, reductive elimination, radical recombination, dissociative adsorption, and so on. An advantage of the “first principles” or logical approach is that there is an enhanced potential for finding reaction mechanisms that otherwise would escape notice. After X and Y become specific species, the program

considers all possible second steps in a similar way. The "space" of possible pathways is simply the set of possible lists of such elementary steps. The only unchangeable built-in assumption in MECHEM is that all elementary steps have at most two reactants and at most two products.

The program organizes its search in stages of simplicity, by first trying to find mechanisms that involve fewer species and steps. A chemist/user drives the process by supplying assumptions, based on experimental evidence and background knowledge. These assumptions are in the form of constraints whose templates (about 120) are implemented and available for use.

*Pathway/catalyst generation.* To explore coking pathways in conformity with our source energetics data,<sup>4</sup> we formulated the starting materials as CH<sub>4</sub>(ads) and CO<sub>2</sub>(ads) and the sole target product as monoatomic carbon. These species and all intermediates or by-products below are actually surface species, although their notation will not indicate this fact.

We made use of the 82 elementary steps (forward and reverse, totaling 164) and their activation energies over eight single-crystal transition metal catalysts reported by the cited authors. MECHEM was constrained to reject any generated step or species that was not on this list. Thus, there were  $8 \times 164 = 1312$  separate activation energies or step/catalyst pairs.

To simplify the task, we excluded any step/catalyst pair whose activation energy exceeded 30 kcal/mol; these would be much less likely to enable good coking pathways. Thus, a new constraint was added to MECHEM that rejects any complete (or partially-constructed) pathway whose steps cannot all take place on one metal and still remain below the energy ceiling. Thus, a sequence whose first step was within the energy ceiling only for metals Fe and Ni, and whose second step was within ceiling only for Pt and Pd, would be discarded because their intersection was empty. The alternative would be to run the program once for each catalyst under consideration; but considering them jointly turns out to be more convenient.

*Pathway selection criteria.* We chose four measures of the likelihood that a pathway will lead to substantial coking; in all four cases, smaller values are better: (1) the number of pathway species; (2) the number of pathway steps; (3) for a specific metal, the maximum activation energy appearing in the pathway; (4) the maximum possible stoichiometric yield of carbon obtainable through the pathway, expressed as the *cost* in moles of CH<sub>4</sub> and CO<sub>2</sub> required to form 1 mole of surface carbon.

For the task of catalyst ranking, the preference for more concise pathways (having fewer species or steps) is justified as follows. The fewer pathway species, the fewer the opportunities for side reactions that diverge from coking; given  $N$  species, there are  $N^2$  formally possible bimolecular and  $N$  unimolecular steps. In this article we do not include an explicit measure of the potential for side reactions, but a preference for fewer pathway species can deal somewhat with this issue.

The preference for fewer steps is justified by the uncertainty in the calculated activation energies. The more steps, the greater the chances of an (undetected) inaccuracy that would render bad a seemingly good pathway. If mistakes in the calculated energies occur with probability  $p$  and are independent, then the probability of a mistake for a pathway of length  $L$  equals  $1 - (1 - p)^L$  which approaches unity exponentially with pathway length.

Measures of the pathway energy barrier more elaborate than a simple *maximum* could be used, and we have experimented with several of them, but here we opt for the simplest choice. The use of maximum activation barriers to characterize pathways assumes that the pathway step with the highest barrier is the slowest. The principled choice of slowest steps should be based on knowledge of surface species concentrations and preexponential factors, but these data are not available.

Finally, we need a measure of *how much* coking can be achieved via a given pathway. Lacking data on reaction rates, we will use a heuristic measure of "selectivity" that is based only on the plain pathway: the maximum possible yield of surface carbon that can be obtained by freely varying the pathway stoichiometric numbers, but keeping them non-negative. The problem of finding the maximum possible yield can be formulated as a linear optimization problem and solved with the simplex algorithm.<sup>12</sup> The basic ideas are to require one mole of carbon after a time  $t_1$ , to express the possible concentration changes in terms of the stoichiometries of the individual steps, and then to minimize the "cost" (i.e., the molar amounts) of starting materials at the prior time  $t_0$ . A by-product of the optimization is a stoichiometric number for each pathway step.

However, there is a subtlety in the cost measure. Since some steps are below the energy ceiling of 30 kcal/mol in both directions, we score pathways in two ways: (1) keeping the original forward direction of steps, and (2) augmenting the pathway with all the reversed steps that are within the energy ceiling. In the latter case, the *maximum energy* measure is calculated over the step directions that correspond to the positive stoichiometric numbers as determined by the linear optimization. If a stoichiometric number is zero, we consider the energy only of the forward direction.\*

\* This tactic is not absolutely correct, since it is possible that a more limited use of backward steps will lead to the most advantageous combination of energy and cost, in the sense of enabling a pathway to survive the comparisons described in the next section. However, given the small sizes of our pathways, we believe that this omission is not important.

*Combining measures.* We know of no principled way to combine these four measures or objectives into a single optimizable objective. However, since the formulation is equivalent to a multi-objective optimization problem, we can use the standard concept of a Pareto optimum. A Pareto optimum is a solution which is not dominated by any other solution; one solution dominates another if it is better on one of the objectives and is no worse on all the other objectives.

Thus, we will find all the Pareto optima, that is, those pathway/catalyst pairs that are not dominated by any other pair in the sense of minimizing the four objectives of steps, species, energy, and cost. We will iterate this procedure several times: after finding the first set (depth 0) of Pareto-optimal pathway/catalyst pairs, we will delete these solutions and all supersets of any of these pathways that involve the same catalyst and do not improve the score along one of the measures; then we collect the (depth 1) Pareto optima among the remaining pathway/catalyst pairs. By carrying out this procedure several times to a depth of 1 or 2, combined with deleting a metal after its place in the ranking is determined, we will obtain a ranked list of good coking pathway/catalyst pairs, together with its justification in terms of explicit coking pathways.

*Generating pathways of increasing complexity.* MECHEM's task is to generate all the simplest (fewest species or steps) mechanisms that can form the declared products or intermediates from the starting materials, while respecting any user-specified constraints. (Here, the constraints are that (1) only steps from our list of 164 elementary steps are allowed, and (2) the activation energy of any directed step must be within 30 kcal/mol.) However, we need to generate not just the simplest mechanisms, but all mechanisms over some range of complexity.

One *reject-supersets* approach to this problem was used earlier:<sup>6</sup> after finding  $N$  simplest mechanisms, an artificial constraint is activated which rejects any future mechanism that contains within itself any of the  $N$  previous mechanisms. At the next run the program will not stop after finding the same  $N$  mechanisms, but instead will search for more complex mechanisms that are guaranteed a degree of novelty with respect to the previous runs. The *reject-supersets* approach has a drawback, though. Consider the schematic pathway  $A \rightarrow X + Y$ ,  $2X \rightarrow T$ , which has four species, two steps, some maximum activation energy, and a cost in the starting material of  $A$  equal to 2. No more complex pathway will be allowed to contain this two-step pathway, so the three-step pathway  $A \rightarrow X + Y$ ,  $2X \rightarrow T$ ,  $Y \rightarrow X$  will never be considered, even though its cost would be reduced to 1 from the previous 2. (Of course, the steps are increased and the maximum activation energy could rise.) Thus, it is possible that we could miss a good pathway.

A second approach to the problem of generating more complex pathways is simply to reject any future mechanism that contains exactly  $S$  species and  $R$  steps, where  $S$  and  $R$  describe the last batch of pathways found. This *more-complex-pathways* approach avoids the cited drawback of the *reject-supersets* approach, but suffers from a potential combinatorial explosion in the number of pathways.

The entire procedure, while somewhat detailed, has been largely automated and is the same from one reaction to the next.

## RESULTS

We generated coking pathways by repeatedly using the *more-complex-pathways* approach until a run generated over one thousand pathways; then we switched to the *reject-supersets* approach. We continued collecting pathways up to a limit of seven species not counting  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{C}$ . The result was a total of 11678 pathways (all the computations were done in a few hours on a 300 MHz, 64Mb laptop computer).

Each pathway was evaluated according to the four measures *steps*, *species*, *energy*, and *cost* over each of the eight catalysts. As explained above, sometimes a pathway/catalyst pair gave rise to two sets of scores, depending on whether pathway steps were allowed to have positive stoichiometric numbers in the backwards direction. The total ensuing number of pathway/catalyst scores was 99267.

The first three sets of Pareto-minimal pathways are shown below. Each step is annotated with its activation energy, and following the listed metal are the scores: number of extra *species*, number of *steps*, maximum activation *energy* barrier, and the minimum *cost* in moles of starting material that is stoichiometrically obtainable via the pathway.

---

### Depth 0

1.  $\text{CO}_2$  -[4.5]  $\rightarrow$  O + CO
  2.  $2(\text{CO})$  -[0.9]  $\rightarrow$   $\text{CO}_2$  + C
- Fe, species = 2, steps = 2, energy = 4.5, cost = 1

### Depth 1

1.  $\text{CO}_2$  -[6.7]  $\rightarrow$  O + CO
  2.  $2(\text{CO})$  -[6.4]  $\rightarrow$   $\text{CO}_2$  + C
- Ni, species = 2, steps = 2, energy = 6.7, cost = 1

### Depth 2

1.  $\text{CH}_4$  +  $\text{CO}_2$  -[8.1]  $\rightarrow$  HCOO +  $\text{CH}_3$
2. HCOO -[3.2]  $\rightarrow$  OH + CO
3.  $\text{CO}_2$  + OH -[3.5]  $\rightarrow$  HCOO + O

4.  $2(\text{CO}) - [0.9] \rightarrow \text{CO}_2 + \text{C}$   
Fe, species = 5, steps = 4, energy = 8.1, cost = 1

1.  $\text{CH}_4 + \text{CO}_2 - [8.1] \rightarrow \text{HCOO} + \text{CH}_3$

2.  $\text{HCOO} - [3.2] \rightarrow \text{OH} + \text{CO}$

3.  $2(\text{CO}) - [0.9] \rightarrow \text{CO}_2 + \text{C}$

Fe, species = 4, steps = 3, energy = 8.1, cost = 3

1.  $\text{CO}_2 - [12.7] \rightarrow \text{O} + \text{CO}$

2.  $2(\text{CO}) - [3.9] \rightarrow \text{CO}_2 + \text{C}$

Ru, species = 2, steps = 2, energy = 12.7, cost = 1

---

We judged that Fe is the single best coking metal, because it possesses the best overall solution (at depth 0) and is backed up by two more pathways at depth 2 that, unlike the first solution, make use of interactions between  $\text{CH}_4$  and  $\text{CO}_2$ . The next step is to delete Fe from further consideration and consider the seven remaining metals.

After Fe, the best catalyst appears to be Ni, which is followed in turn by Ru. After repeated minimizations to some depth, followed by excluding from further consideration the metals which we judged to be the next best, we obtained the results summarized below.

---

*Take all metals*

Depth 0: 1 Fe pathway  $\Rightarrow$  Depth 1: 1 Ni pathway  $\Rightarrow$  Depth 2: 2 Fe and 1 Ru pathways

Conclude: Fe is best. Exclude Fe

Depth 0: 1 Ni pathway  $\Rightarrow$  Depth 1: 3 Ru and 1 Rh pathways  $\Rightarrow$  Depth 2: 18 pathway/catalyst pairs (5 Ni)

Conclude: Ni is best after Fe. Exclude Fe, Ni

Depth 0: 3 Ru and 1 Rh pathways

Conclude: Ru is best after Fe, Ni. Exclude Fe, Ni, Ru

Depth 0: 23 pathways (9 Ir, 8 Pd, 6 Rh)

Conclude: Ir, Pd, Rh are best after Fe, Ni, Ru. Exclude Fe, Ni, Ru, Ir, Pd, Rh

Depth 0: 10 pathways (8 Pt, 2 Cu)

Conclude: Pt, Cu are the two worst

---

Our overall ranking of metals based on this detailed analysis of coking pathways is: Fe > Ni > Ru > Rh ~ Ir ~ Pd > Cu ~ Pt. Thus, according to the available elementary steps and activation energies, Fe and Ni favor coke formation the most, and Cu and Pt the least.

## DISCUSSION

*Comparison of results with literature.* Coke deposition on metals from both  $\text{CH}_4$  and  $\text{CO}_2$  or their mixtures is a very complex process.<sup>13,14</sup> Catalyst resistance to coking strongly depends on the nature of the support<sup>15,16</sup> and promoters,<sup>17,18</sup> which is one reason why direct comparisons of coking for various transition metals have not been carried out. Another reason is that noble metals are expensive and industry prefers to use promoted nickel catalysts instead, which are the focus of most studies. So, there is scarce experimental precedence for comparing our predictions to empirical results.

The only reliable qualitative conclusion about carbon deposition in  $\text{CO}_2$  reforming of methane that we are able to discern from numerous experimental investigations is that the noble metals (Pd, Rh, Ru, Ir, and Pt) are generally less susceptible to coke deposition than Fe, Co, and Ni.<sup>19</sup> Our findings are in complete agreement with this pattern, as well as with the data that stability of carbides decreases from iron to nickel, with copper carbide unknown.<sup>20</sup>

Interestingly, Trimm<sup>9</sup> discusses an activity pattern Fe > Ni > noble metals for steam reforming that is consonant with our results and with the cited pattern of Arutyunov and Krylov.<sup>19</sup> This consonance supports the Rostrup-Nielsen conjecture that the steps of both mechanisms are similar.<sup>21</sup>

*Limitations.* We have not considered coke removal, only its formation. The data on activation energies<sup>4</sup> suggest that the coke-removal rate must be very high: the activation energies for the step  $\text{CO}_2 + \text{C} \rightarrow \text{CO} + \text{CO}$  are zero for Cu, Ni, Pd, Pt, Rh, and Ir, 1.1 for Ru, and 6.1 kcal/mol for Fe. The Pareto-minimal pathways show that the highest energy barriers among coke formation steps are usually higher. Thus, the lowest (most competitive) energy barrier of the Pareto-minimal pathway at depth 0 is 4.5 kcal/mol. This suggests that coke formation is competitive with coke removal only on Fe (4.5 vs. 6.1 kcal/mol), whereas coke is removed faster than it is formed on the other metals. This obviously contradicts the common knowledge that on Ni, coke is formed faster than it is removed, which is why promoters are used in Ni-based catalysts. Assuming that relative activation energies are a satisfactory heuristic guide to the relative rates of steps, we conjecture that carbon polymerization on the surface and carbon-metal phase formation are faster processes than coke removal. Thus, the monoatomic carbon formed in our coking pathways is consumed by these fast, undesirable processes. So, the more that a pathway/catalyst pair favors coke formation, the more chances that the catalyst will be poisoned with coke.

We did not consider adsorption/desorption steps, which may slightly affect the result.

We are considering only the formation of monoatomic surface carbon, and not the solubility of carbon in the bulk of the metal. The available information on the solubility of carbon in metals somewhat correlates with our ranking of metals: Fe > Ni > noble metals<sup>19</sup> and Rh > Pd > Ru > Ir > Pt (maximum solubility data)<sup>20</sup>. Also, the data reported by Hei *et al.*<sup>4</sup> were calculated at zero coverage and we inherit this limitation. A future step will be to re-calculate all the data at higher coverages and refine current data.

Of course, real catalysts are more complicated, due to nonzero surface coverage effects, formation of various carbon-metal phases, carbon dissolution in the bulk, diffusion processes, transformations of monoatomic carbon into polymeric carbon and vice versa, and so on. However, to the extent that some of these complicating effects can be captured in the formulation of elementary steps and their energetic barriers, our method will be able to accommodate them.

Finally, we also neglected preexponential factors and did not try to simulate the kinetics of any of these pathways. Further step will be to estimate preexponential factor using transition state theory.

## CONCLUSIONS

We have proposed the combinatorial generation of pathway/catalyst pairs, screened for conciseness, energetics, and stoichiometry, as a computational method for ranking alternative catalysts with respect to a given target property, here, coking in CO<sub>2</sub> reforming of methane. The input to the method is a list of possible elementary steps and their energetics, and the output is a ranking of catalysts augmented with pathway-oriented justifications for the ranking. Rankings and pathways such as these can complement other approaches to catalyst design, e.g., those whose assumed starting point is a serviceable reaction mechanism.

We also started the work on the future use of this method for the ranking of metals in the main reaction: CO<sub>2</sub> + CH<sub>4</sub> → CO + H<sub>2</sub> and on improving the selectivity and activity criteria. One of these criteria is based on the calculation of the apparent activation energy as a function of the surface coverages for intermediate species. Preliminary results of this work show that Ir, Ru, and Rh are best among eight catalyst considered here. Cu, Pd, and Pt are worse than others. Fe and Ni hold an intermediate position.

Our findings on metal catalyst coking for CO<sub>2</sub> reforming are relevant to steam reforming since the list of steps is largely identical for both processes.<sup>21</sup>

## REFERENCES

- (1) Somorjai, G. A.; Zaera, F. *J. Phys. Chem.* **1982**, *86*, 3070.
- (2) Cardenas-Galindo, M.; Aparicio, L. M.; Rudd, D. F.; Dumesic, J. A. In *Computer-Aided Design of Catalysts*; Becker, E.; Pereira, C., Eds.; Marcel Dekker: New York, 1993.
- (3) Zeigarnik, A. V.; Valdes-Perez, R. E.; Temkin, O. N. *Langmuir* **1998**, *14*, 4510.
- (4) Hei, M. J.; Chen, H. B.; Yi, J.; Lin, Y. J.; Lin, Y. Z.; Wei, G.; Liao, D. W. *Surf. Sci.* **1998**, *417*, 82.
- (5) Becker, E.; Pereira, C. In *Computer-Aided Design of Catalysts*; Becker, E.; Pereira, C., Eds.; Marcel Dekker: New York, 1993.
- (6) Zeigarnik, A. V.; Valdes-Perez, R. E.; Temkin, O. N.; Bruk, L. G.; Shalgunov, S. I. *Organometallics* **1997**, *16*, 3114.
- (7) Bruk, L. G.; Gorodskii, S. N.; Zeigarnik, A. V.; Valdes-Perez, R. E.; Temkin, O. N. *J. Mol. Catal. A: Chem.* **1998**, *130*, 29.
- (8) Zeigarnik, A. V.; Valdes-Perez, R. E.; White, B. S. *J. Chem. Educ.*, in press.
- (9) Trimm, D. L. *Design of Industrial Catalysts*; Elsevier: New York, N.Y., 1980.
- (10) Shustorovich, E.; Sellers, H. *Surf. Sci. Rep.* **1998**, *31*, 1.
- (11) (a) Valdes-Perez, R. E. *J. Comput. Chem.* **1992**, *13*, 1079; (b) Valdes-Perez, R. E. *J. Comput. Chem.* **1993**, *14*, 1454; (c) Valdes-Perez, R. E. *J. Comput. Chem.* **1994**, *15*, 1266.
- (12) Valdes-Perez, R. E. *J. Phys. Chem.* **1991**, *95*, 4918.
- (13) Rostrup-Nielsen, J. R. In *Catalysis - Science and Technology*, Vol. 5; Anderson, J.; Boudart, M., Eds.; Springer Verlag: Berlin, 1984.
- (14) Bradford, M. C. J.; Vannice, M. A. *Catal. Rev. - Sci. Eng.* **1999**, *41*, 1.
- (15) Bradford, M. C. J.; Vannice, M. A. *Appl. Catal. A: General* **1996**, *142*, 73.
- (16) Sodesawa, T.; Dobashi, A.; Nozaki, F. *React. Kinet. Catal. Lett.* **1979**, *12*, 107.
- (17) Trimm, D. L. *Catal. Today* **1999**, *49*, 3.
- (18) Haliche, D.; Bourab, R.; Cherifi, O.; Bettahar, M. M. *Catal. Today* **1996**, *29*, 373.
- (19) Arutyunov, V. S.; Krylov, O. V. *Oxidative Conversion of Methane*; Nauka: Moscow, 1998 (in Russian).
- (20) Joyner, R. W.; Darling, G. R.; Pendry, J. B. *Surf. Sci.* **1988**, *205*, 513.
- (21) Rostrup-Nielsen, J. R.; Bak Hansen, J. H. *J. Catal.* **1993**, *144*, 38.
- (22) Savitskii, E. M.; Polykova, V. P.; Gorina, N. B.; Roshan, N. R. *Physical Metallurgy of Platinum Metals*; Moscow: Metallurgiya, 1975 (in Russian).