

# Alternative Algebraic Perspectives on CO/H<sub>2</sub> PROX over MnO<sub>2</sub> Composite Catalysts

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## GCODE: How to use it

The example provided is currently addressed to the referees of the article of the header. It constitutes an example to extract, using GCODE, information regarding the PROX catalytic system at  $T = 298$  K and a total pressure of 100 kPa, with the percentages of CO, O<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> being 1, 1, 98, and 0, respectively. However, it could also be applied to the study of other complex catalytic cycles by modifying the input related to the energetic information and adapting the graph representation to these new cycles.

GCODE for modularity and simplicity, is here shaped by two environments named WATER and FIRE. In the first, given a starting graph, representing a catalytic mechanism, the

spanning tree ( $\Sigma$ -T) and the cycle branched component (X-T) LISP lists needed for the analysis are individuated. In the second this analysis is performed extracting the catalytic information.

The WATER environment is formed by four component codes: **W0**, **W1**, **W2**, **W3**. The former identifies the possible branches, X-Ts, that connect to the different cycles present in the graph. **W0** is also included in this repository although it is extremely simple to extract the component X-Ts of the branched graphs, reported in Figs. 4 and 5 of the title article, through a visual analysis of the starting graph related to the catalytic mechanism. The remaining codes are applied, in the order, **W1**, **W2** and **W3**. In this work the result of this procedure is summarized by Table S2, including the 62 tuples representing the spanning trees characterizing the whole process considered. These do not include neither cycles nor reversible edges and show all the edges oriented to one of the nodes in the graph (*e.g.*, see Fig. 3).

**W1** is employed to extract all the isolable  $\Sigma$ -Ts (in this case 78 graphs). To get this result, **W1** receive as input the information of the file **graphD\_in** summing up the list of edges representing the steps of the whole catalytic mechanism. Whereas, to reach the final information on the 62  $\Sigma$ -Ts, **W2** operates on **sink\_out-1**, the file output of **W1** containing the tuple representation of the 78 spanning trees including the ones containing cycles as well as reversible edges, and **W3** on the one, **sink\_out\_0**, of **W2**, containing the filtered 54 spanning trees not containing internal cycles but still including reversible edges. Of course, the results obtained in the WATER environment do not depend on the temperature.

The FIRE environment is formed by three components, *i.e.* **F1**, **F2** and **F3**. The file **T298**, input of **F1**, contains the values of  $\Delta G^\ddagger$  reported in Table S1 for the involved steps, which are individuated following the node notation reported in Fig. 2(a). The  $\Delta G^\ddagger$  values for the steps involving adsorption processes have been additionally corrected using Eq. 3 at the given temperature, total pressure, and partial pressures considered.

The component code **F1** reads information from the file **T298** and loads the files **W2\_0**,

**W2\_1 – W2\_12** and **C2** and **C3**. The first contains the graphs of all the  $\Sigma$ -T lists, expressed as tuples of edges, characterizing the overall mechanism. The same  $\Sigma$ -Ts are separately grouped, as shown in Table S2, in the files **W2\_1 – W2\_12** while **C3** and **C2** contain the same information, although referring to the branched cycles of Figs. 4 and 5. These files are all processed, and the result is collected in the corresponding **END\_X** files with  $X = 0 - 12, C2, C3$ , which gather the related overall weights of the  $\Sigma$ -Ts and branched cycles, expressed in terms of Total Energy Content (TEC/kJmol<sup>-1</sup>) values. Each  $TEC = \sum_k \Delta G_k^\ddagger$  is clearly related to each considered subgraph (either a spanning tree or a branched cycle), with  $k$  representing any edge/step component of the latter.

The component **F2** is a bridge code that processes the information in the **END\_X** files and returns the corresponding files **EXIT\_X**, with  $X = 0 - 12, C2, C3$ . These files collect in a compact form (*i.e.* without redundant information) the tuples of the TEC values for each group of  $\Sigma$ -Ts and branched graphs.

The component **F3** reads the files **EXIT\_X** and processes them, generating the complementary **RESULT\_X** files, which report the cumulative probabilities, corresponding to the product of the exponential kernels present in Eqs. 2 and 3, characteristic of the  $\Sigma$ -Ts and branched graphs, containing X-Ts. This information, through Eqs. 5, 7, and 8, enables the calculation of TOF values, surface populations and selectivity, for the given temperature and pressures.

It can be noted that all the **END**, **EXIT** and **RESULTS** files, if present, can be safely erased and easily regenerated while the component codes can be linked through a batch file. In order to calculate the properties of the same system at different temperatures only the **F3** component needs to be modified, introducing the new temperature. Finally, to evaluate the effects of the pressure of the gas phase species, useful for example in determining the reaction orders, the values of  $\Delta G^\ddagger$  for the steps involving adsorption processes in the file **T**, in this case **T298**, must be corrected through Eq. 4.