

Alternative Algebraic Perspectives on CO/H₂ PROX over MnO₂ 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, H₂, O₂, and N₂ 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 (Σ -T) and the branched cycle (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 that connect the different cycles present in the graph, in order to pinpoint the X-T components. **W0** is not included in this repository because it is extremely simple to extract the branched X-Ts, 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, to extract all the isolable Σ -Ts. In this work the result of this procedure is summarized by Table 3. To obtain the reported data, **W1** receive as input the information of the file **graphD_in** summing up the list of edges representing the whole catalytic mechanism. To get the final information on the Σ -Ts, **W2** operates on **sink_out-1**, the file output of **W1**, and **W3** on the one, **sink_out_0**, of **W2**. 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 ΔG^\ddagger reported in Table 1 for the involved steps, which are individuated following the node notation reported in Fig. 2(b). The ΔG^\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 Σ -T lists, expressed as tuples of edges, characterizing the overall mechanism. The same Σ -Ts are separately grouped, as shown in Table 3, in the files **W2_1** – **W2_12** while **C3** and **C2** contain the same information, although referring to the branched X-Ts 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 Σ -Ts and X-Ts, expressed in terms of Total Energy Content (TEC/kJmol⁻¹) values, being $TEC = \sum_k \Delta G_k^\ddagger$.

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 tuples of TEC values for each group of Σ -Ts and X-Ts.

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. 1 and 2, characteristic of the Σ -Ts and X-Ts. This information, through Eqs. 4, 6, and 7, 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 ΔG^\ddagger for the steps involving adsorption processes in the file **T**, in this case **T298**, must be corrected through Eq. 3.