

The implementation of a surface mechanism for NO oxidation, NOx storage, and NOx desorption over Pt/BaO/Al₂O₃ using Chemkin utilities.

Author:

Anthony McDaniel

Sandia National Laboratories

e-mail: amcdani@sandia.gov

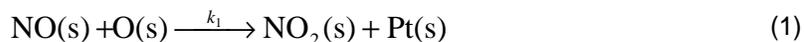
This document describes the implementation of a surface mechanism for NO oxidation, NOx storage, and NOx desorption over Pt/BaO/Al₂O₃ using Chemkin utilities. The reaction network was taken from *Olsson et al., J. Phys. Chem. B 2001, 105, 6895-6906* and translated from a pseudo first-order turnover frequency (TOF) formalism to a mass action rate law formalism which is more suitable for utilization within Chemkin applications. This distribution includes Chemkin input files, a fortran user routine, raw data digitized from the article, and example output from a transient perfectly-stirred reactor (PSR) simulation. In addition, a detailed description of the mapping between TOF and mass action expressions is supplied, along with a short narrative on implementing surface diffusion of adsorbed NO₂ between Pt and BaO active sites, described by Olsson et al. to account for spillover effects, but which cannot be directly resolved within the PSR model. The example problem makes use of Chemkin 3.7.1 and assumes familiarity with this software. For more information regarding Chemkin please consult the URL www.reactiondesign.com.

Archive contents:

File Name	Description
aurora_user_routines.f	fortran routine for user-supplied input into AURORA
Pt_BaO_mech.inp	surface reaction mechanism
no_gas.inp	gas phase mechanism
psr_PtBaO.inp	AURORA keyword input
psr_PtBaO.out	text output from example calculation
Olsson_PtBaO.csv	comma-delimited file of raw data
trans.txt	text file read into AURORA through fortran routine
XML_psr.zip	archived solution file from example calculation

Mapping TOF kinetic expressions to mass action:

In the Olsson article, the authors make use of fractional surface coverage as the conserved quantity in the rate equations that govern adsorbate-adsorbate, adsorbate-surface, and vapor-surface interactions. For example, the rate of adsorbed NO reacting with adsorbed O expressed conceptually as



where (s) denotes a surface specie, can be given by the following ordinary differential equation

$$\left[\begin{array}{c} 1 \\ -s \end{array} \right] \frac{d\theta_{\text{NO(s)}}}{dt} = -k_1 \theta_{\text{NO(s)}} \theta_{\text{O(s)}} \quad (2)$$

where θ_i is the fraction of the surface covered by species i , and k_1 in this case a pseudo first-order rate constant that takes the Arrhenius form and carries a 1/time unit (hence the expression turn over frequency). If the rate equation is then weighted by the moles of active sites per mass of catalyst, one obtains the units reported by Olsson et al. in the tabulation of their kinetic model (see paper). Equation (2) can also be expressed in terms of surface concentration units (mol/cm² s) according to

$$\left[\frac{\text{mol}}{\text{cm}^2 \text{ s}} \right] \frac{d[\text{NO}(s)]}{dt} = -k_1'[\text{NO}(s)][\text{O}(s)] \quad (3)$$

where the following relationships between concentration, surface coverage, and rate constants are defined for a simple reaction that is first order in species concentration (or coverage)

$$\left[\frac{\text{mol}}{\text{cm}^2} \right] [X_i] = \frac{Z_i \Gamma_n}{\sigma_i(n)}, \quad [\text{unitless}] \theta_i = \frac{Z_i}{\sigma_i(n)}, \quad \sum_i Z_i = 1, \quad k_1' = \frac{k_1}{\Gamma_n}$$

where X_i is the surface concentration, Z_i is the surface site fraction (different than coverage), Γ_n is the active site density (mol sites/cm²) for phase (n), and $\sigma_i(n)$ is the surface site occupation number for species i in phase (n) ($\theta_i = Z_i$ in the limit of unit site occupation). Converting the rate constant from TOF to mass action space is straight forward for eq. (1), however, it can be quite complicated for reactions that involve different site densities (as is the case with NO₂ transport between Pt and BaO), when site occupation numbers are greater than unity, and when reactions are not first order in species (or coverage). In addition to unit conversion, there is an added level of complexity associated with coverage-dependent activation energy in the Arrhenius expression that is used by Olsson et al. This feature is supported within Chemkin and adequately detailed in the user manuals.

Chemkin surface reaction mechanism:

To develop the Chemkin-compatible version of the Olsson et al. mechanism, active site densities for Pt and BaO must be assigned. In this treatment, two materials will be defined CATALYST (Pt) and STORAGE (BaO). For Pt, the site density is given by Olsson et al. as $\Gamma_{Pt} = 2.08 \times 10^{-9}$ mol Pt/cm². For BaO, the theoretical site density is estimated from the lattice constant ($a = 5.539 \text{ \AA}$) of the simple cubic primitive cell.

$$\Gamma_{BaO} = \frac{0.5 \text{ Ba}^{++} \text{ atoms}}{(5.539 \text{ \AA})^2} \left| \frac{(10^8 \text{ \AA})^2}{\text{cm}^2} \right| \frac{\text{mol}}{6.02 \times 10^{23} \text{ atoms}} = 2.71 \times 10^{-10} \text{ mol Ba / cm}^2$$

Incidentally, the same calculation for face-centered cubic Pt ($a = 3.92 \text{ \AA}$ and 2 atoms per cell) yields $\Gamma_{Pt} = 2.16 \times 10^{-9}$ mol Pt/cm². Next, the pre-exponential factors are stripped of catalyst weight dependence (returned to pseudo first-order units), divided through by active site density, and then modified to account for any residual constants arising from coverage dependence in the modified Arrhenius expression used by Olsson et al. The following example calculation typifies this procedure (for k_1 from Table 2 in Olsson et al., reaction on Pt sites):

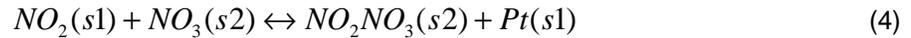
$$k_1 = 6.6 \times 10^2 \text{ (m}^3/\text{s kg catalyst)} \cdot \exp(-30.4/RT)$$

$$k_1 = \frac{6.6 \times 10^2 \text{ m}^3}{\text{s kg catalyst}} \left| \frac{\text{kg catalyst}}{3.8 \times 10^{-3} \text{ mol}} \right| \left| \frac{(100)^3 \text{ cm}^3}{\text{m}^3} \right| \frac{\text{cm}^2}{2.08 \times 10^{-9} \text{ mol}} = \frac{8.35 \times 10^{19} \text{ (cm}^5/\text{s mol}^2)}{\exp(-30.4/RT)}$$

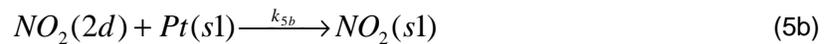
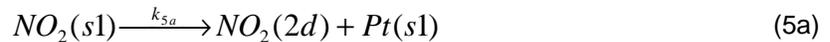
There are certainly more complicated examples where Olsson et al. have chosen a modified Arrhenius expression, using a reference temperature to center the rate constant, as well as coverage dependent activation energies. These examples can be identified in the input file (see Pt_BaO_mech.inp) by the use of additional keywords such as "COV"; please refer to the Chemkin manuals for usage and clarification. A word of caution with the use of "COV" and "REV", Chemkin only allows coverage dependence for forward reactions thus making "COV" and "REV" incompatible. For example, in order to properly apply coverage dependence to the reverse reaction in eq. (15) [Olsson et al.], the user must define the reaction set as a pair of irreversible steps (see Pt_BaO_mech.inp).

Surface transport of NO₂(s) from Pt to BaO:

In order to account for spillover effects between Pt and BaO, Olsson et al. postulated the following reaction, which would be better represented by a surface diffusion term in the governing equations:



where (s1) is the CATALYST and (s2) the STORAGE material, respectively. Beside the conceptual difficulty of describing surface diffusion as a reaction between adsorbates, converting to a mass action formalism involves making a choice between which surface site density to use when dividing through the pre-exponential constant. In addition, a ratio of site densities must then be carried through the governing ODEs for this process in order for the system of equations to conserve mass. Therefore to avoid confusion, two separate materials (CATALYST and STORAGE) were defined at the outset. Since Chemkin treats materials as independent entities, it is up to the user to define a means of communication between the two (e.g. a surface diffusion submodel). Unfortunately, the AURORA Chemkin application in release 3.7.1 cannot account for surface diffusion, therefore transport will have to be accomplished through a gas-phase intermediate. Here, the net result of eq. (4) can be represented by a set of 4 irreversible reactions, two occurring in each of the defined materials:



where $NO_2(2d)$ is a volatile specie that only interacts with either $Pt(s1)$ or $NO_3(s2)$. One can envision $NO_2(2d)$ locally hopping from CATALYST to STORAGE and back again. The behavior represented by eq. (4) is then recovered by equating k_{5a} to r_{19} [Olsson et al.], k_{5c} to r_{20} [Olsson et al.], and assuming $k_{5b} \gg k_{5a}$ and $k_{5d} \gg k_{5c}$. By judicious choice of pre-exponential factors for k_{5b} and k_{5d} such that the gas-phase concentration of $NO_2(2d)$ is small (near machine round-off) but not small enough to cause numerical instabilities, the system of equations (5a to 5d) adequately represents eq. (4).

AURORA solution:

To simulate the transient NOx storage problem outlined by Olsson et al., use the input files supplied with this archive and follow instructions in the Chemkin manuals for rebuilding AURORA with the supplied user subroutine. The problem specifications for AREA, AFRA *material*, and VOL were first taken directly from the Olsson paper. However, better agreement was obtained by adjusting AREA and AFRA. This archive includes the raw data set digitized from Olsson et al., which can be imported directly into the Chemkin post processor for comparison with simulation results, as well as the XML zip archive of my solution.