Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Micro-kinetic Simulations of the Catalytic Decomposition of Hydrazine on the Cu (111) Surface

Saeedeh S. Tafreshi,[1] Alberto Roldan,[2] Nora H. de Leeuw[1,2]*

[1] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
[2] School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK
**Corresponding author. Tel.: +44 2920870658. E-mail address:* DeLeeuwN@cardiff.ac.uk.

The accuracy in determining the energy is further improved by correcting the static DFT electronic energy using the zero point energies. The zero point energy (ZPE) accounts for the vibrational energy that exists even at 0 K and is calculated as $ZPE = \sum \frac{1}{2} h \nu_i$ where ν_i corresponds to the vibrational modes of the species. To obtain more accurate results we have considered the effect of the temperature on E_{ads}, E_r and E_a and corrected them by a temperature dependent parameter. Thus, energy as a function of temperature for each different system can be calculated using the global partition function, *Q*, and several relevant physical parameters such as entropy (S), specific heat at constant pressure (C_p) and enthalpy (*H*) derived with the following equations; [1, 2]

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_V \tag{S1}$$

$$C_p = T \left[\frac{\partial S}{\partial T} \right]_p \tag{S2}$$

$$H = E_{DFT} + E_{(S=0, T=0, ZPE)} + \int_0^T C_p \partial T \tag{S3}$$

$$G = H - TS \tag{S4}$$

The thermodynamic properties of the intermediates on the surface or in the gas phase were calculated using the above equations. Fig. S1 shows both the calculated and NIST database [3] thermodynamic properties of NH_3 while the free energy of N_2, H_2 is shown in Fig. S2. Table S1 contains the relative error of the derived properties compared with the extracted datas from Shomate equations in the NIST database [3].

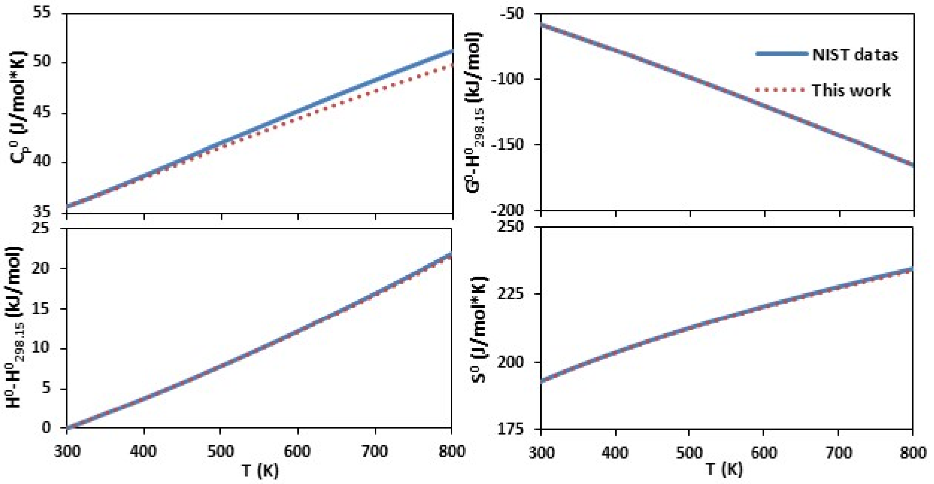

Fig. S1. Calculated thermodynamic properties of NH_3 in the gas phase compared with the NIST database [3].

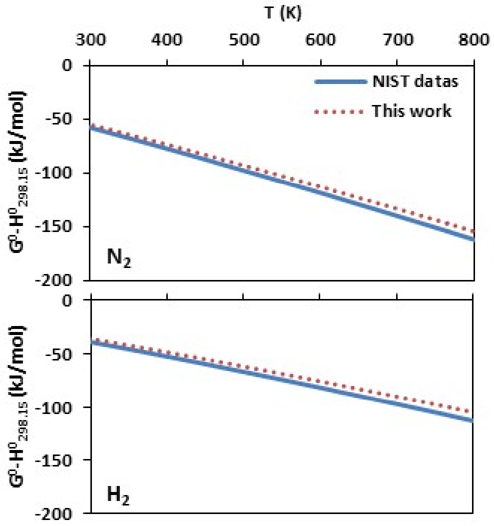

Fig. S2. Calculated thermodynamic properties of N_2 and H_2 in the gas phase compared with NIST database [3].

Table S1. Relative errors (in %) of the calculated thermodynamic properties of NH_3, N_2 and H_2 in the gas phase compared with the NIST database [3].

	$(Cp^0_{cal.}-Cp^0_{NIST}/Cp^0_{NIST})*100$	$(S^0_{cal.}-S^0_{NIST}/S^0_{NIST})*100$	$(H^0_{cal.}-H^0_{NIST}/H^0_{NIST})*100$	$(G^0_{cal.}-G^0_{NIST}/G^0_{NIST})*100$
NH_3	-1.37	-0.13	-0.76	-0.08
N_2	-0.48	-4.55	-0.30	-4.82
H_2	-0.61	-6.76	-0.42	-7.33

We consider the global partition function as the product of the partition functions:

$$Q = q_{translational} \cdot q_{rotational} \cdot q_{vibrational} \cdot q_{electronic} \cdot q_{nuclear} \tag{S5}$$

We have included translational, rotational, vibrational, electronic and nuclear contributions in the partition functions. Usually the electronic systems are in a singlet electronic state, and the nuclear partition functions are unity [2].

The vibrational partition function of a system [4] is obtained via,

$$q_{vib} = \prod_{i=1}^{N} \frac{1}{1 - e^{-h\nu_i / k_B T}} \tag{S6}$$

Where, *i* is a specific vibrational mode and N is the number of vibrations. The vibrational partition function in the gas phase, q_{vib}^{gas}, is also calculated using the equation above for $3N_i - 6$ and $3N_i - 5$ vibrational degrees of freedom of a non-linear and linear molecule in the gas phase, respectively, where N_i is the number of atoms in the molecule.

The 2D-translational partition function for a free molecule is derived by the Eq (S7);

$$q_{trans}^{2D} = \frac{2\pi m k_B T}{h^2} A_{cat} \tag{S7}$$

The Rotational partition function for a free molecule is calculated using Eqs (S8) or (S9) depending on its symmetry;

$$q_{rot}^{linear} = \frac{1}{\sigma} \frac{8\pi I k_B T}{h^2} \tag{S8}$$

$$q_{rot}^{nonlinear} = \frac{1}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{\pi I_a I_b I_c} \tag{S9}$$

Where σ is the symmetry factor and *I* is the moment of inertia defined as $I = \mu r^2$, being μ the reduced mass and *r* the atom distances to the centre of mass (CM).

In the heterogeneous catalytic system, the constant rate (k) of each surface elementary step is commonly computed using the transition-state theory (TST) approximation of Eyring [5] and Evans and Polanyi [6], as follows;

$$k = A_0 \exp\left(\frac{-\Delta G^{\neq}}{k_B T} \right) = \frac{k_B T}{h} \frac{q_{TS}}{q_{IS}} \exp\left(\frac{-\Delta G^{\neq}}{k_B T} \right) \tag{S10}$$

Where h is the Plank constant, k_B is the Boltzmann constant, T is the temperature, A_0 is the pre-exponential factor, $\Delta G^{\neq}$ is the reaction activation energy and; q_{IS} and q_{TS} are the partition functions of reactants and transition states respectively.

The translations and rotations of the adsorbed species are frustrated on the surface and therefore we considered only vibrational modes [2].

In the case of the desorption processes, the partition function q_{IS} includes only the vibrational frequencies, while q_{TS} is the partition function for the transition state, which we have considered as in direct adsorption, see below.

There are two types of adsorption, direct and indirect; the direct adsorption implies that the molecule lands immediately at its final adsorption site and stays at the point of impact as an adsorbed species while in indirect adsorption, molecule adsorbs via a physisorbed precursor and after some time in this state, it finds a free site to bond to the surface [2]. We have considered the direct adsorption for molecules through this work. The rate of an adsorption process is estimated from the classical Hertz-Knudsen equation [7], Eq (S11);

$$k_{ads,i} = A_0 S_0 = \frac{A_{cat}}{\sqrt{2\pi m_i k_B T}} S_0(T) \tag{S11}$$

Where A_0 is the pre-exponential factor, A_{cat} is the area of one free site (3.87×10^{-19} m^2 in this work) and the sticking coefficient, $S_0(T)$, is a measure of the fraction of incident molecules which adsorb upon the surface and is calculated via Eq (S12);

$$S_0(T) = \frac{q_{vib}^{TS}}{q_{trans}^{2D} q_{rot}^{gas} q_{vib}^{gas}} \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{S12}$$

Where the incident-free molecule moves perpendicularly to the surface towards a transition state (TS) which is anchored. Hence, its translation and rotation are frustrated and its partition function includes only vibration, q_{vib}^{TS}, derived from Eq (S6), from which the reaction coordinate, perpendicular to the surface, has been excluded. ΔE is the energy difference between the free molecule and the molecule in the transition state [2]. In Eq (S12), the q_{trans}^{2D} is the 2D-translational partition function for the free molecule derived by the Eq (S7), where the third frustrated translational mode vanishes since it is the reaction coordinate. The rotational partition function for a free molecule, q_{rot}^{gas}, is calculated using Eqs (S8) or (S9) depending on its symmetry.

We have considered an active site as a hexagonal site made up from 7 Cu atoms where the reactants and products in every elementary step occupy only one site on the surface. Consequently, the coverage of free sites, $\theta_*(t)$, is defined by;

$$\theta_*(t) = 1 - \sum_i^n \theta_i(t) \tag{S13}$$

Where the $\theta_i(t)$ represents the coverage of the intermediates present in the reaction system.

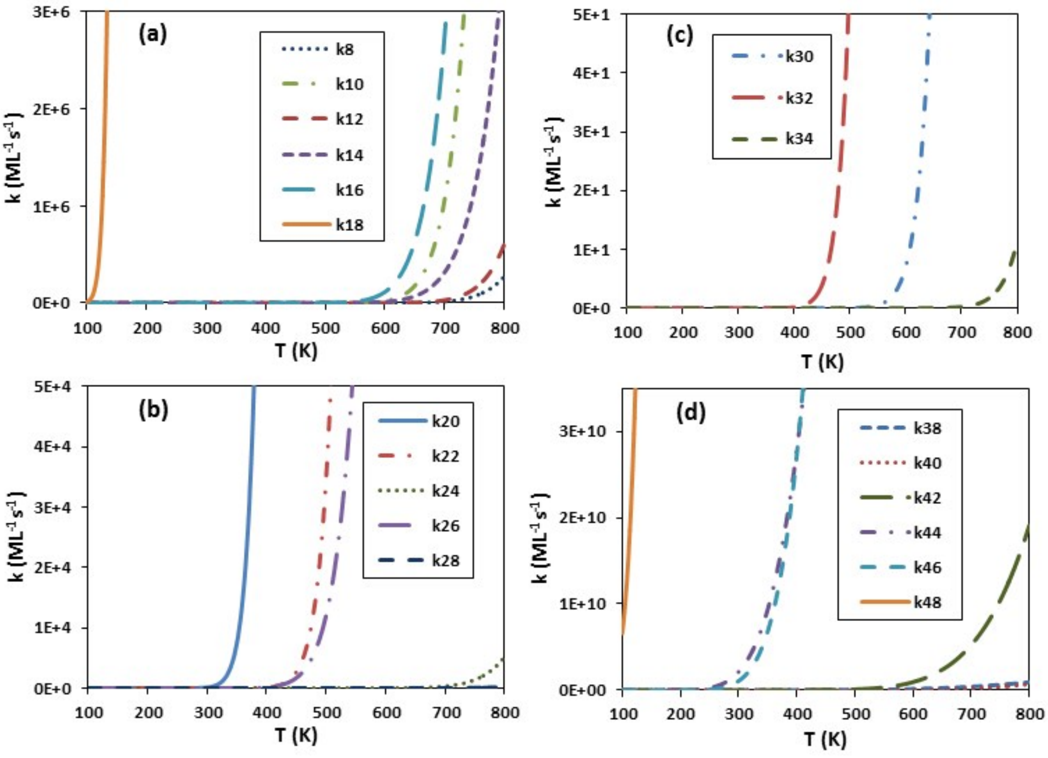

Fig. S3. Calculated reaction rate constants (k) as a function of temperature (T) for reactions of, (a) N_2H_x (x=1-4) dehydrogenation, (b) N_2H_x (x=1-4) N–N decoupling, (c) NH_x (x=1-3) dehydrogenation and, (d) interaction of NH_2 with N_2H_x (x=1-4) mechanisms.

The following are the rate equations of the elementary reactions applied in the simulations of hydrazine decomposition on the Cu(111) surface.

$$r_0(t) = \frac{A}{\sqrt{2\pi m_{N_2H_4} k_B T}} \frac{q_0^{TS}}{q_0^{IS}} e^{-\frac{E_0^a}{k_B T}} P_{N_2H_4}(t)\theta_*(t)$$

$$r_1(t) = \frac{k_B T}{h} \frac{q_1^{TS}}{q_1^{IS}} e^{-\frac{E_1^a}{k_B T}} \theta_{N_2H_4}(t)$$

$$r_2(t) = \frac{k_B T}{h} \frac{q_2^{TS}}{q_2^{IS}} e^{-\frac{E_2^a}{k_B T}} \theta_{NH_3}(t)$$

$$r_3(t) = \frac{A}{\sqrt{2\pi m_{NH_3} k_B T}} \frac{q_3^{TS}}{q_3^{IS}} e^{-\frac{E_3^a}{k_B T}} P_{NH_3}(t)\theta_*(t)$$

$$r_4(t) = \frac{k_B T}{h} \frac{q_4^{TS}}{q_4^{IS}} e^{-\frac{E_4^a}{k_B T}} \theta_{N_2}(t)$$

$$r_5(t) = \frac{A}{\sqrt{2\pi m_{N_2} k_B T}} \frac{q_5^{TS}}{q_5^{IS}} e^{-\frac{E_5^a}{k_B T}} P_{N_2}(t)\theta_*(t)$$

$$r_6(t) = \frac{k_B T}{h} \frac{q_6^{TS}}{q_6^{IS}} e^{-\frac{E_6^a}{k_B T}} \theta_H^2(t)$$

$$r_7(t) = \frac{A}{\sqrt{2\pi m_{H_2} k_B T}} \frac{q_7^{TS}}{q_7^{IS}} e^{-\frac{E_7^a}{k_B T}} P_{H_2}(t) \theta_*(t)$$

$$r_8(t) = \frac{k_B T}{h} \frac{q_8^{TS}}{q_8^{IS}} e^{-\frac{E_8^a}{k_B T}} \theta_{N_2H_4}(t)$$

$$r_9(t) = \frac{k_B T}{h} \frac{q_9^{TS}}{q_9^{IS}} e^{-\frac{E_9^a}{k_B T}} \theta_{N_2H_3}(t) \theta_H(t)$$

$$r_{10}(t) = \frac{k_B T}{h} \frac{q_{10}^{TS}}{q_{10}^{IS}} e^{-\frac{E_{10}^a}{k_B T}} \theta_{N_2H_3}(t)$$

$$r_{11}(t) = \frac{k_B T}{h} \frac{q_{11}^{TS}}{q_{11}^{IS}} e^{-\frac{E_{11}^a}{k_B T}} \theta_{NNH_2}(t) \theta_H(t)$$

$$r_{12}(t) = \frac{k_B T}{h} \frac{q_{12}^{TS}}{q_{12}^{IS}} e^{-\frac{E_{12}^a}{k_B T}} \theta_{N_2H_3}(t)$$

$$r_{13}(t) = \frac{k_B T}{h} \frac{q_{13}^{TS}}{q_{13}^{IS}} e^{-\frac{E_{13}^a}{k_B T}} \theta_{NHNH}(t) \theta_H(t)$$

$$r_{14}(t) = \frac{k_B T}{h} \frac{q_{14}^{TS}}{q_{14}^{IS}} e^{-\frac{E_{14}^a}{k_B T}} \theta_{NNH_2}(t)$$

$$r_{15}(t) = \frac{k_B T}{h} \frac{q_{15}^{TS}}{q_{15}^{IS}} e^{-\frac{E_{15}^a}{k_B T}} \theta_{NNH}(t) \theta_H(t)$$

$$r_{16}(t) = \frac{k_B T}{h} \frac{q_{16}^{TS}}{q_{16}^{IS}} e^{-\frac{E_{16}^a}{k_B T}} \theta_{NHNH}(t)$$

$$r_{17}(t) = \frac{k_B T}{h} \frac{q_{17}^{TS}}{q_{17}^{IS}} e^{-\frac{E_{17}^a}{k_B T}} \theta_{NNH}(t) \theta_H(t)$$

$$r_{18}(t) = \frac{k_B T}{h} \frac{q_{18}^{TS}}{q_{18}^{IS}} e^{-\frac{E_{18}^a}{k_B T}} \theta_{NNH}(t)$$

$$r_{19}(t) = \frac{k_B T}{h} \frac{q_{19}^{TS}}{q_{19}^{IS}} e^{-\frac{E_{19}^a}{k_B T}} \theta_{N_2}(t) \theta_H(t)$$

$$r_{20}(t) = \frac{k_B T}{h} \frac{q_{20}^{TS}}{q_{20}^{IS}} e^{-\frac{E_{20}^a}{k_B T}} \theta_{N_2H_4}(t)$$

$$r_{21}(t) = \frac{k_B T}{h} \frac{q_{21}^{TS}}{q_{21}^{IS}} e^{-\frac{E_{21}^a}{k_B T}} \theta_{NH_2}^2(t)$$

$$r_{22}(t) = \frac{k_B T}{h} \frac{q_{22}^{TS}}{q_{22}^{IS}} e^{-\frac{E_{22}^a}{k_B T}} \theta_{N_2H_3}(t)$$

$$r_{23}(t) = \frac{k_B T}{h} \frac{q_{23}^{TS}}{q_{23}^{IS}} e^{-\frac{E_{23}^a}{k_B T}} \theta_{NH_2}(t) \theta_{NH}(t)$$

$$r_{24}(t) = \frac{k_B T}{h} \frac{q_{24}^{TS}}{q_{24}^{IS}} e^{-\frac{E_{24}^a}{k_B T}} \theta_{NNH_2}(t)$$

$$r_{25}(t) = \frac{k_B T}{h} \frac{q_{25}^{TS}}{q_{25}^{IS}} e^{-\frac{E_{25}^a}{k_B T}} \theta_{NH_2}(t) \theta_N(t)$$

$$r_{26}(t) = \frac{k_B T}{h} \frac{q_{26}^{TS}}{q_{26}^{IS}} e^{-\frac{E_{26}^a}{k_B T}} \theta_{NHNH}(t)$$

$$r_{27}(t) = \frac{k_B T}{h} \frac{q_{27}^{TS}}{q_{27}^{IS}} e^{-\frac{E_{27}^a}{k_B T}} \theta_{NH}^2(t)$$

$$r_{28}(t) = \frac{k_B T}{h} \frac{q_{28}^{TS}}{q_{28}^{IS}} e^{-\frac{E_{28}^a}{k_B T}} \theta_{NNH}(t)$$

$$r_{29}(t) = \frac{k_B T}{h} \frac{q_{29}^{TS}}{q_{29}^{IS}} e^{-\frac{E_{29}^a}{k_B T}} \theta_{NH}(t) \theta_N(t)$$

$$r_{30}(t) = \frac{k_B T}{h} \frac{q_{30}^{TS}}{q_{30}^{IS}} e^{-\frac{E_{30}^a}{k_B T}} \theta_{NH_3}(t)$$

$$r_{31}(t) = \frac{k_B T}{h} \frac{q_{31}^{TS}}{q_{31}^{IS}} e^{-\frac{E_{31}^a}{k_B T}} \theta_{NH_2}(t) \theta_H(t)$$

$$r_{32}(t) = \frac{k_B T}{h} \frac{q_{32}^{TS}}{q_{32}^{IS}} e^{-\frac{E_{32}^a}{k_B T}} \theta_{NH_2}(t)$$

$$r_{33}(t) = \frac{k_B T}{h} \frac{q_{33}^{TS}}{q_{33}^{IS}} e^{-\frac{E_{33}^a}{k_B T}} \theta_{NH}(t) \theta_H(t)$$

$$r_{34}(t) = \frac{k_B T}{h} \frac{q_{34}^{TS}}{q_{34}^{IS}} e^{-\frac{E_{34}^a}{k_B T}} \theta_{NH}(t)$$

$$r_{35}(t) = \frac{k_B T}{h} \frac{q_{35}^{TS}}{q_{35}^{IS}} e^{-\frac{E_{35}^a}{k_B T}} \theta_N(t) \theta_H(t)$$

$$r_{36}(t) = \frac{k_B T}{h} \frac{q_{36}^{TS}}{q_{36}^{IS}} e^{-\frac{E_{36}^a}{k_B T}} \theta_{NH_2}^2(t)$$

$$r_{37}(t) = \frac{k_B T}{h} \frac{q_{37}^{TS}}{q_{37}^{IS}} e^{-\frac{E_{37}^a}{k_B T}} \theta_{NH}(t) \theta_{NH_3}(t)$$

$$r_{38}(t) = \frac{k_B T}{h} \frac{q_{38}^{TS}}{q_{38}^{IS}} e^{-\frac{E_{38}^a}{k_B T}} \theta_{N_2H_4}(t) \theta_{NH_2}(t)$$

$$r_{39}(t) = \frac{k_B T}{h} \frac{q_{39}^{TS}}{q_{39}^{IS}} e^{-\frac{E_{39}^a}{k_B T}} \theta_{N_2H_3}(t) \theta_{NH_3}(t)$$

$$r_{40}(t) = \frac{k_B T}{h} \frac{q_{40}^{TS}}{q_{40}^{IS}} e^{-\frac{E_{40}^a}{k_B T}} \theta_{N_2H_3}(t)\theta_{NH_2}(t)$$

$$r_{41}(t) = \frac{k_B T}{h} \frac{q_{41}^{TS}}{q_{41}^{IS}} e^{-\frac{E_{41}^a}{k_B T}} \theta_{NHNH}(t)\theta_{NH_3}(t)$$

$$r_{42}(t) = \frac{k_B T}{h} \frac{q_{42}^{TS}}{q_{42}^{IS}} e^{-\frac{E_{42}^a}{k_B T}} \theta_{N_2H_3}(t)\theta_{NH_2}(t)$$

$$r_{43}(t) = \frac{k_B T}{h} \frac{q_{43}^{TS}}{q_{43}^{IS}} e^{-\frac{E_{43}^a}{k_B T}} \theta_{NNH_2}(t)\theta_{NH_3}(t)$$

$$r_{44}(t) = \frac{k_B T}{h} \frac{q_{44}^{TS}}{q_{44}^{IS}} e^{-\frac{E_{44}^a}{k_B T}} \theta_{NHNH}(t)\theta_{NH_2}(t)$$

$$r_{45}(t) = \frac{k_B T}{h} \frac{q_{45}^{TS}}{q_{45}^{IS}} e^{-\frac{E_{45}^a}{k_B T}} \theta_{NNH}(t)\theta_{NH_3}(t)$$

$$r_{46}(t) = \frac{k_B T}{h} \frac{q_{46}^{TS}}{q_{46}^{IS}} e^{-\frac{E_{46}^a}{k_B T}} \theta_{NNH_2}(t)\theta_{NH_2}(t)$$

$$r_{47}(t) = \frac{k_B T}{h} \frac{q_{47}^{TS}}{q_{47}^{IS}} e^{-\frac{E_{47}^a}{k_B T}} \theta_{NNH}(t)\theta_{NH_3}(t)$$

$$r_{48}(t) = \frac{k_B T}{h} \frac{q_{48}^{TS}}{q_{48}^{IS}} e^{-\frac{E_{48}^a}{k_B T}} \theta_{NNH}(t)\theta_{NH_2}(t)$$

$$r_{49}(t) = \frac{k_B T}{h} \frac{q_{49}^{TS}}{q_{49}^{IS}} e^{-\frac{E_{49}^a}{k_B T}} \theta_{N_2}(t)\theta_{NH_3}(t)$$

$$r_{50}(t) = \frac{k_B T}{h} \frac{q_{50}^{TS}}{q_{50}^{IS}} e^{-\frac{E_{50}^a}{k_B T}} \theta_{N_2}(t)$$

$$r_{51}(t) = \frac{k_B T}{h} \frac{q_{51}^{TS}}{q_{51}^{IS}} e^{-\frac{E_{51}^a}{k_B T}} \theta_{N}^2(t)$$

Differential equations in the TPR simulation:

$$\frac{dP_{N_2H_4}}{dt} = r_1$$

$$\frac{dP_{NH_3}}{dt} = r_2$$

$$\frac{dP_{N_2}}{dt} = r_4$$

$$\frac{dP_{H_2}}{dt} = r_6$$

$$\frac{d\theta_{N_2H_4}}{dt} = -r_1 + r_9 - r_8 + r_{21} - r_{20} + r_{39} - r_{38}$$

$$\frac{d\theta_{NH_3}}{dt} = -r_2 + r_{31} - r_{30} + r_{38} - r_{39} + r_{40} - r_{41} + r_{42} - r_{43} + r_{44} - r_{45} + r_{46} - r_{47} + r_{48} - r_{49}$$

$$\frac{d\theta_{N_2}}{dt} = -r_4 + r_{51} - r_{50} + r_{48} - r_{49} + r_{18} - r_{19}$$

$$\frac{d\theta_{N_2H_3}}{dt} = r_8 - r_9 + r_{11} - r_{10} + r_{13} - r_{12} + r_{23} - r_{22} + r_{38} - r_{39} + r_{41} - r_{40} + r_{43} - r_{42}$$

$$\frac{d\theta_{NNH_2}}{dt} = r_{10} - r_{11} + r_{15} - r_{14} + r_{25} - r_{24} + r_{42} - r_{43} + r_{47} - r_{46}$$

$$\frac{d\theta_{NHNH}}{dt} = r_{12} - r_{13} + r_{17} - r_{16} + r_{27} - r_{26} + r_{40} - r_{41} + r_{45} - r_{44}$$

$$\frac{d\theta_{NNH}}{dt} = r_{14} - r_{15} + r_{16} - r_{17} + r_{19} - r_{18} + r_{29} - r_{28} + r_{44} - r_{45} + r_{46} - r_{47} + r_{49} - r_{48}$$

$$\frac{d\theta_{NH_2}}{dt} = 2r_{20} - 2r_{21} + r_{22} - r_{23} + r_{24} - r_{25} + r_{30} - r_{31} + r_{33} - r_{32} + 2r_{37} - 2r_{36} + r_{39} - r_{38} + r_{41} - r_{40}$$
$$+ r_{43} - r_{42} + r_{45} - r_{44} + r_{47} - r_{46} + r_{49} - r_{48}$$

$$\frac{d\theta_{NH}}{dt} = r_{22} - r_{23} + 2r_{26} - 2r_{27} + r_{28} - r_{29} + r_{32} - r_{33} + r_{35} - r_{34} + r_{36} - r_{37}$$

$$\frac{d\theta_{N}}{dt} = r_{24} - r_{25} + r_{28} - r_{29} + r_{34} - r_{35} + 2r_{50} - 2r_{51}$$

$$\frac{d\theta_{H}}{dt} = -2r_{6} + r_{8} - r_{9} + r_{10} - r_{11} + r_{12} - r_{13} + r_{14} - r_{15} + r_{16} - r_{17} + r_{18} - r_{19} + r_{30} - r_{31}$$
$$+ r_{32} - r_{33} + r_{34} - r_{35}$$

Differential equations in the batch reactor simulation:

$$\frac{dP_{N_2H_4}}{dt} = r_1 - r_0$$

$$\frac{dP_{NH_3}}{dt} = r_2 - r_3$$

$$\frac{dP_{N_2}}{dt} = r_4 - r_5$$

$$\frac{dP_{H_2}}{dt} = r_6 - r_7$$

$$\frac{d\theta_{N_2H_4}}{dt} = r_0 - r_1 + r_9 - r_8 + r_{21} - r_{20} + r_{39} - r_{38}$$

$$\frac{d\theta_{NH_3}}{dt} = r_3 - r_2 + r_{31} - r_{30} + r_{38} - r_{39} + r_{40} - r_{41} + r_{42} - r_{43} + r_{44} - r_{45} + r_{46} - r_{47} + r_{48} - r_{49}$$

$$\frac{d\theta_{N_2}}{dt} = r_5 - r_4 + r_{51} - r_{50} + r_{48} - r_{49} + r_{18} - r_{19}$$

$$\frac{d\theta_{N_2H_3}}{dt} = r_8 - r_9 + r_{11} - r_{10} + r_{13} - r_{12} + r_{23} - r_{22} + r_{38} - r_{39} + r_{41} - r_{40} + r_{43} - r_{42}$$

$$\frac{d\theta_{NNH_2}}{dt} = r_{10} - r_{11} + r_{15} - r_{14} + r_{25} - r_{24} + r_{42} - r_{43} + r_{47} - r_{46}$$

$$\frac{d\theta_{NHNH}}{dt} = r_{12} - r_{13} + r_{17} - r_{16} + r_{27} - r_{26} + r_{40} - r_{41} + r_{45} - r_{44}$$

$$\frac{d\theta_{NNH}}{dt} = r_{14} - r_{15} + r_{16} - r_{17} + r_{19} - r_{18} + r_{29} - r_{28} + r_{44} - r_{45} + r_{46} - r_{47} + r_{49} - r_{48}$$

$$\frac{d\theta_{NH_2}}{dt} = 2r_{20} - 2r_{21} + r_{22} - r_{23} + r_{24} - r_{25} + r_{30} - r_{31} + r_{33} - r_{32} + 2r_{37} - 2r_{36} + r_{39} - r_{38} + r_{41} - r_{40}$$
$$+ r_{43} - r_{42} + r_{45} - r_{44} + r_{47} - r_{46} + r_{49} - r_{48}$$

$$\frac{d\theta_{NH}}{dt} = r_{22} - r_{23} + 2r_{26} - 2r_{27} + r_{28} - r_{29} + r_{32} - r_{33} + r_{35} - r_{34} + r_{36} - r_{37}$$

$$\frac{d\theta_{N}}{dt} = r_{24} - r_{25} + r_{28} - r_{29} + r_{34} - r_{35} + 2r_{50} - 2r_{51}$$

$$\frac{d\theta_{H}}{dt} = 2r_{7} - 2r_{6} + r_{8} - r_{9} + r_{10} - r_{11} + r_{12} - r_{13} + r_{14} - r_{15} + r_{16} - r_{17} + r_{18} - r_{19} + r_{30} - r_{31}$$
$$+ r_{32} - r_{33} + r_{34} - r_{35}$$

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