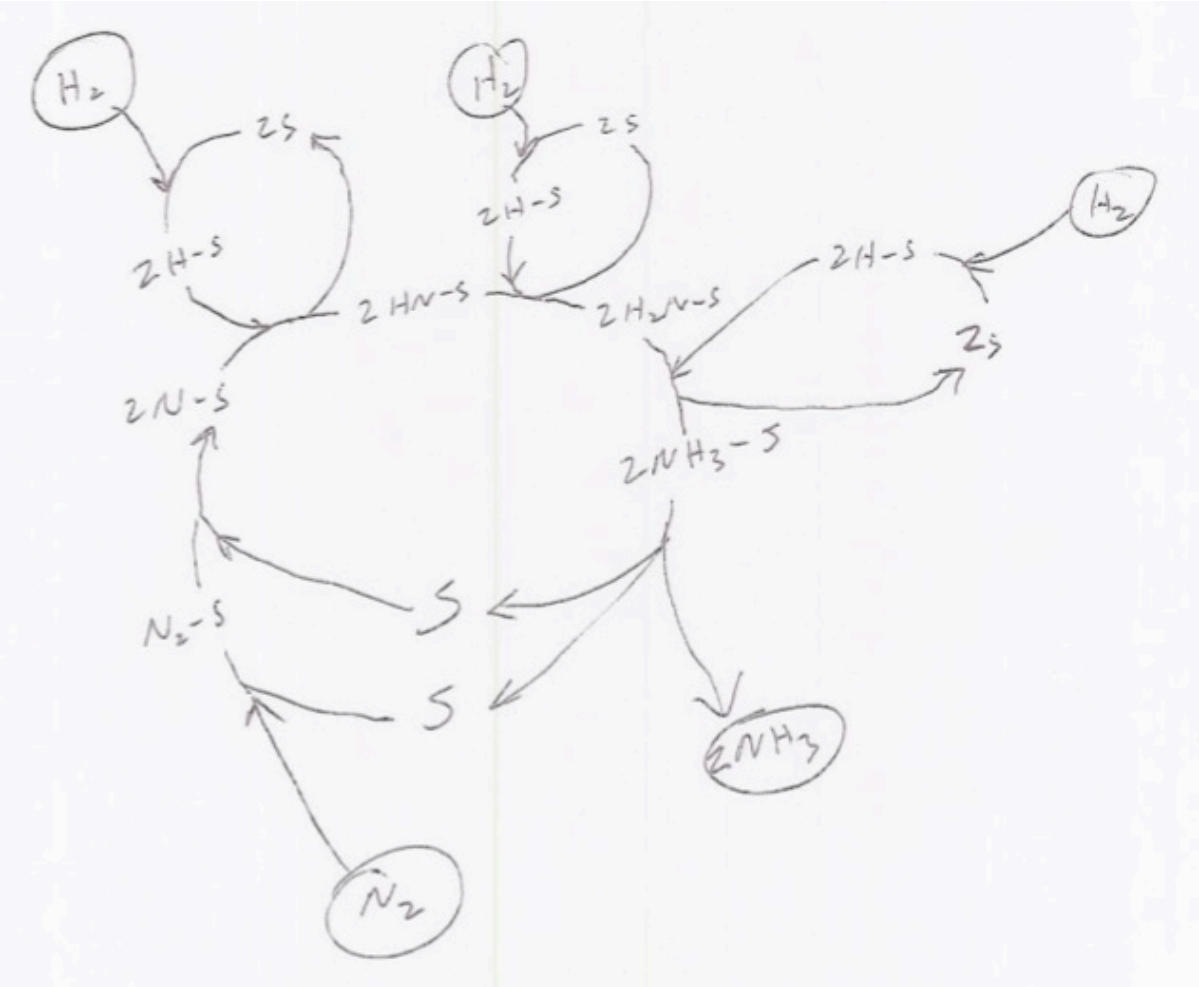
Slides shown in CENG 252, January 11, 2012, R. Herz <herz@ucsd.edu>

The surface-catalyzed ammonia synthesis reaction shown as a catalytic cycle



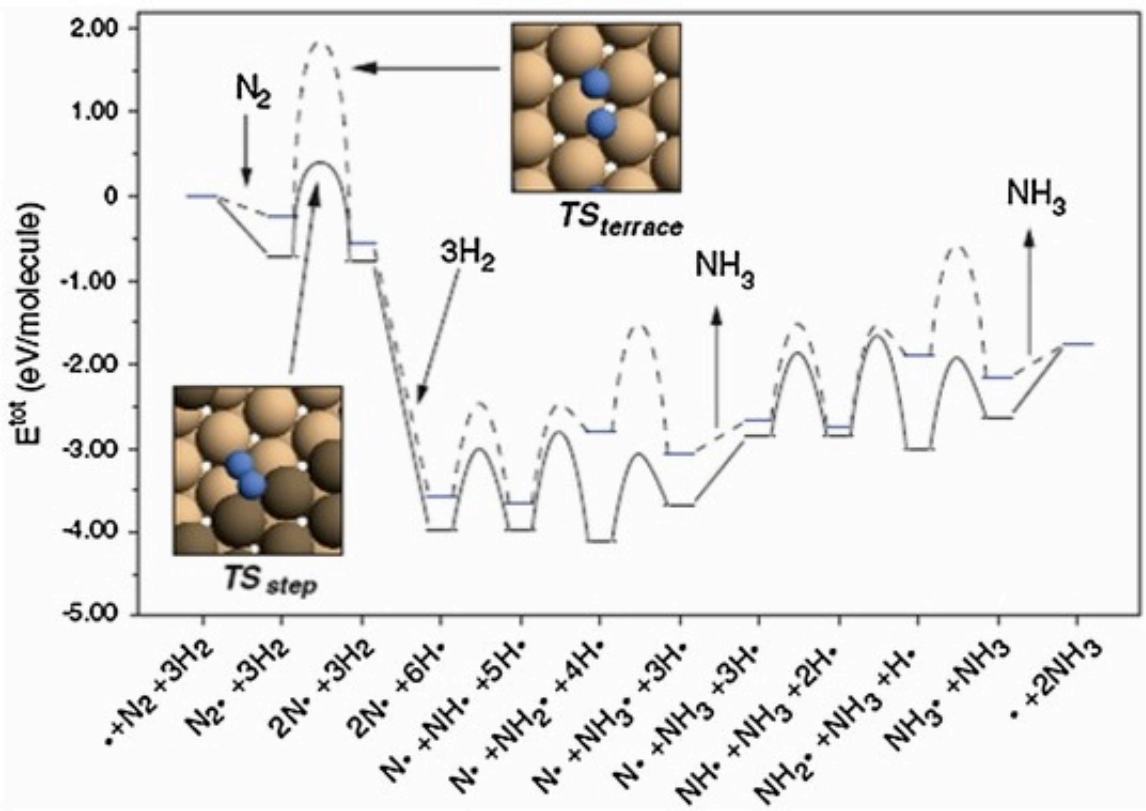
The individual surface sites "S" are not confined to individual subcycles but can participate in different subcycles at different times. The active catalyst in most industrial catalysts is Fe. The sites S represent one or more Fe atoms on the surface. The exact configuration of an adsorbed species over the surface atoms can vary between adsorbed species and one adsorbed species may adsorb over two or more different configurations. For the purpose of developing reaction rate equations for reactor design, it is usually sufficient to assume that S equals one surface Fe atom. There are too many other variables that affect reaction rates in industrial reactors to justify writing a more detailed model.

Energy diagram of the surface-catalyzed ammonia synthesis reaction

Source: G. A. Somorjai and Y. Li, "Major Successes of Theory-and-Experiment-Combined Studies in Surface Chemistry and Heterogeneous Catalysis," *Topics in Catalysis*, vol. 53, no. 5-6, pp. 311-325, Feb. 2010. <http://www.springerimages.com/Images/Chemistry/1-10.1007_s11244-010-9449-0-16>

Note that the overall reaction is exothermic. The initial, reference state on the left is at zero energy for the empty surface + gas-phase N_2 + 3 gas-phase H_2. The final state on the right at lower energy is for the empty surface + 2 gas-phase NH_3 molecules.

For the reaction in the gas phase, the initial and final states would be at the same energies as shown in the figure. A catalyst doesn't change the overall enthalpy or entropy changes. However, for the gas-phase mechanism, the energies of the intermediate states would go off the top of this page.



Caption

Fig 17 The calculated potential energy diagram for ammonia synthesis from N_2 and H_2 over close-packed (001) and stepped Ru surfaces. A * denotes an empty site and X* an adsorbed species. The solid line is for the reaction on a step site, and the dashed line on the terrace. The configurations of the transition states for N_2 dissociation over the terrace and stepped sites are shown in the insets