Catalyst Design by Interpolation in the Periodic Table: Bimetallic Ammonia Synthesis Catalysts

Claus J. H. Jacobsen,*,† Søren Dahl,† Bjerne S. Clausen,†
Sune Bahn,‡ Ashildur Logadottir,‡ and Jens K. Nørskov‡

Haldor Topsøe A/S, Nymøllevej 55
DK-2800 Lyngby, Denmark
Center for Atomic-Scale Materials Physics (CAMP)
Technical University of Denmark, Building 307
DK-2800 Lyngby, Denmark

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Thus far, essentially all heterogeneous catalysts of industrial importance have been developed by trial-and-error experimentation. The classic example of this approach is the discovery of the iron-based ammonia synthesis catalyst by Mittasch and co-workers who tested more than 2500 different catalysts in 6500 experiments.[1,2] Parallel testing methods, which can speed up catalyst screening significantly, have recently been introduced,[3] but a better scientific basis could make catalyst development substantially more efficient.

We show that a rational catalyst development strategy can be developed on the basis of simple, physically motivated concepts. We use the ammonia synthesis reaction to illustrate the approach, but the general principles should be broadly applicable.

The starting point is the volcano-shaped relation between the ammonia synthesis activity of different catalysts and their nitrogen adsorption energy shown in Figure 1. The curve shows (in complete agreement with experimental evidence[4]) that Ru and Os are the best catalysts among the pure metals. The dependence of the catalytic activity on the nitrogen adsorption energy is a consequence of a linear (Brønsted−Evans−Polanyi) relationship[5] between the activation energy for the rate-limiting step, which is N_2 dissociation,[6,7] and the stability of adsorbed N on the surface. The reason for this relationship is that the transition state for N_2 dissociation is very final-state-like. Therefore, the transition-state energy essentially follows the nitrogen adsorption energy from one metal to the next.

The volcano shape of the plot in Figure 1 implies that there is an optimum for the nitrogen adsorption energy. This optimum reflects a compromise between two mutually opposing ways of achieving a high activity: a small activation barrier for N_2 dissociation and a surface with low coverage of adsorbed atomic nitrogen during ammonia synthesis. This requires a strong and a weak N-surface interaction, respectively. At conditions relevant in industrial processes we get closest to the optimum by using Ru or Os as catalysts. However, these metals are very expensive and thus less commercially attractive compared to the third-best catalyst, Fe.

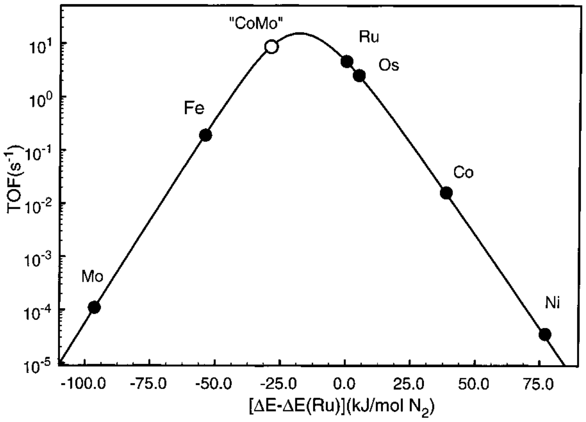

Figure 1. Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen. The synthesis conditions are 400 °C, 50 bar, gas composition H_2:N_2 = 3:1 containing 5% NH_3. The numbers are obtained by combining a microkinetic model describing ammonia synthesis rates with the linear relation existing between the potential energy and the activation energy for N_2 dissociation.[5] The known entropy barrier for N_2 dissociation[20] and the effect of adding electropositive promoters such as K and Cs[21] have been taken into account in the model.

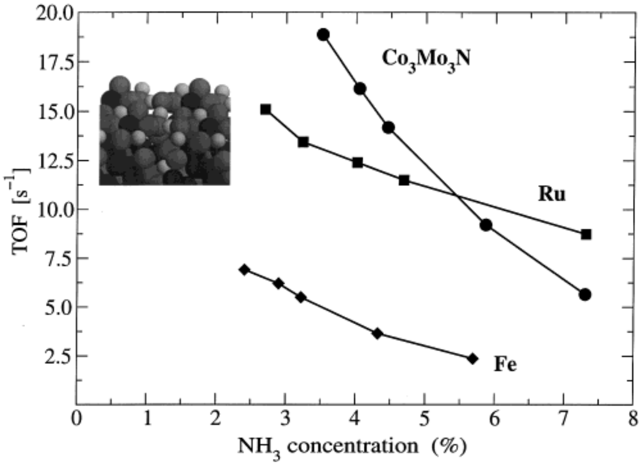

Figure 2. Measured turnover frequencies for promoted Ru, Co_3Mo_3N, and Fe catalysts. The number of active sites is calculated from the surface areas of the active components, assuming that 1% of the total surface sites (10^{19} m^{-2}) are active for N_2 dissociation. (Inset): Surface structure of Co_3Mo_3N showing the existence of mixed Co−Mo sites.[19] Light gray: N; dark gray: Co; black: Mo.

A rational approach could be to construct a surface (active sites) with the desired intermediate nitrogen interaction energy by combining two metals: one with too high adsorption energy and one with too low adsorption energy. As indicated in Figure 1, a combination of Mo (which binds N too strongly) with Co (which binds N too weakly) should be close to optimum. This is exactly what was found experimentally.[8−10] A Co−Mo catalyst was developed using this principle, and it had an ammonia synthesis activity much better than that of the constituents and even better than those of both Fe and Ru at low NH_3 concentrations, see Figure 2. In the following, we will show why this is the case.

We study the chemical behavior of alloy surfaces with mixed-metal sites for ammonia synthesis using plane wave DFT calculations. The RPBE exchange-correlation functional is applied,[11] and Vanderbilt ultrasoft pseudopotentials[12] are used to

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* Corresponding author. Nymøllevej 55, DK-2800 Lyngby, Denmark, Telephone: + 45 45 27 22 02. Fax: + 45 45 27 29 99. E-mail: chj@topsoe.dk.

† Haldor Topsøe A/S.

‡ Center for Atomic-Scale Materials Physics.

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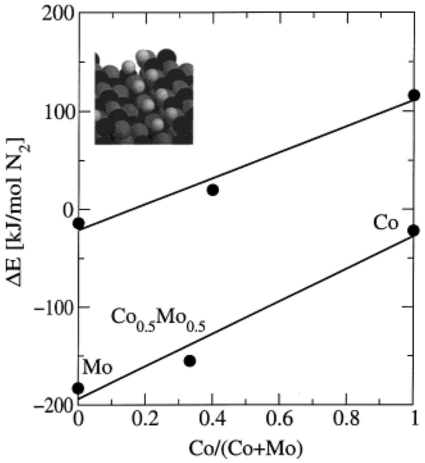

Figure 3. Calculated transition-state energies for N_2 dissociation and nitrogen adsorption energies on Co, $Co_{0.5}Mo_{0.5}$, and Mo close-packed surfaces with a step. The energies are relative to the situation where the N_2 molecule is far from the surface. The geometry of the surface site and the N_2 molecule at the transition state are shown in the insert (for $Co_{0.5}Mo_{0.5}$). Light gray: N; dark gray: Co; black: Mo.

describe the core electrons. The program employed (DACAPO) is publicly available at http://www.fysik.dtu.dk/campos. As illustrated in Figure 3, we use a four-layer hcp(0001) slab with a (4 × 2) surface unit cell to model the active surface of Co and of the CoMo alloy. In the top layer, two rows of atoms are removed to give step sites, since they have been shown theoretically and experimentally to be the active sites for a number of metals[5,13] The lattice constant has been determined by a separate calculation. The results for Mo(110) are from ref 5. The two top layers are completely relaxed in the calculations. The transition states are identified by calculating the energy for various lengths of the N_2 bond, while the remaining degrees of freedom are relaxed.

In Figure 3 we show the calculated barrier for N_2 dissociation and nitrogen adsorption energy on Co, Mo, and $Co_{0.5}Mo_{0.5}$ surfaces. The energies are shown as a function of the relative number of Co neighbors in the active site. The most stable site for atomic N is a three-fold site with one Co and two Mo neighbors, corresponding to a value of $Co/(Co + Mo) = 0.33$. In the transition state, on the other hand, five metal atoms are involved, two Co and three Mo, giving a value of $Co/(Co + Mo) = 0.40$. Clearly the barrier and the N adsorption energy of the alloy is intermediate between that of the constituents. Other sites with other Co concentrations and thus other adsorption energies and barriers will exist. In fact, a distribution of barriers and bond energies will exist for a given distribution of sites in an alloy catalyst surface. As indicated by the results in the figure the activation energies and bond energies are strongly correlated, and the different sites will correspond to different points along the volcano curve of Figure 1. The points closest to the maximum will contribute most to the measured rate.

We suggest this is a quite general phenomenon: to a first approximation the interaction energy between an adsorbate and the surface at a mixed site is simply an interpolation between the interaction energies of the individual components. Consequently, other combinations of metals are also expected to have N adsorption energies close to the optimum and thus higher activity than their constituents. For Fe−Ru and Fe−Co alloys,[14,15] and for ternary nitrides[8] Ni_2Mo_3N and Co_3Mo_3N, this has been observed experimentally. If the interpolation concept is applied for other reactions, the alloy with bimetallic active sites only has higher activity than the constituents when the catalytic activity is a nonlinear function of the interaction energy, as for reactions with a volcano-type relationship.

For the active site of the mixed-metal catalyst to have the interpolated properties, it is important that both metals are present in close proximity at the surface. This is not always the case. Usually one of the components will segregate to the surface either as a consequence of the properties of the binary alloy or because one of the components binds strongly to the adsorbates on the surface. If there is a tendency toward ordering in the alloy, such effects may be suppressed.[16] The alloy catalyst that was tested, compare Figure 2, is a ternary nitride with the composition Co_3Mo_3N. The (111) surface of Co_3Mo_3 (ref 19), shown as an inset in Figure 2, displays the existence of mixed Co−Mo surface sites in the nitride structure. Microkinetic modeling and isothermal N_2 adsorption experiments show[17] that the activation energy and N-binding energy of Cs/Co_3Mo_3N are intermediate between those of Co and Mo. Furthermore, the adsorption experiments confirm that the bulk nitrogen of the ternary nitride does not participate in the reaction. Consequently, the primary role of the nitrogen atoms in the ternary nitride catalyst is to induce the required ordering. The small content of nitrogen in the bulk is not believed to significantly affect other properties.[18]

Preparation of ammonia synthesis catalysts by combining metals with high and low nitrogen interaction energies to obtain the desired intermediate interaction strength is an example of a rational approach to catalyst design. Since the nitrogen binding energies on different metals vary monotonically with the position of the metal in the Periodic Table, the present approach is an example of catalyst design by interpolation in the Periodic Table.

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