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# Why the optimal ammonia synthesis catalyst is not the optimal ammonia decomposition catalyst

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## Abstract

Developments in ammonia synthesis have also made it possible to take a more rational approach to research on ammonia decomposition. It has been found that the optimal catalyst for ammonia synthesis is never the optimal catalyst for ammonia decomposition, which is almost counter-intuitive in catalysis research. The approach taken for ammonia synthesis/decomposition could be useful for many other systems and lead to a more rational development of new and improved catalysts and catalytic processes.

*Keywords:* Ammonia decomposition; Ammonia synthesis; DFT; Heterogeneous catalysis; Kinetics

## 1. Introduction

The design of catalysts for ammonia decomposition is an interesting challenge, since this reaction can be used for on-site hydrogen generation in proton-exchange membrane fuel cells [1,2]. This appears to be an attractive alternative to producing hydrogen from carbonaceous substances, because hydrogen can be produced without the production of carbon monoxide impurities that will poison the fuel cell anode [3] and without poisoning the environment [4]. In such a scenario, practical and safer ways of transporting ammonia are required, as are more efficient ammonia decomposition catalysts.

Research on ammonia decomposition is traditionally strongly related to research on ammonia synthesis. Today, the catalytic synthesis of ammonia is the heterogeneous catalytic reaction of which we have the most detailed understanding [5]. Concepts developed for catalytic ammonia synthesis can be applied to catalytic ammonia decomposition and help predict the properties of the optimal decomposition catalysts. The principle of microscopic reversibility suggests that under a given set of reaction conditions the ammonia decomposition rate, $r_{\mathrm{decomp}}$, can be written as

$$r_{\mathrm{decomp}} = r_{\mathrm{syn}} \frac{p_{\mathrm{NH_3}}^2}{p_{\mathrm{N_2}} p_{\mathrm{H_2}}^3 K_{\mathrm{eq}}} \equiv r_{\mathrm{syn}} \beta.$$

Here $r_{\mathrm{syn}}$ is the ammonia synthesis rate, $K_{\mathrm{eq}}$ is the equilibrium constant for ammonia synthesis, $p_x$ is the partial pressure of species $x$, and $\beta$ is the approach to equilibrium. This relation could suggest that the optimal ammonia synthesis catalyst is also the optimal ammonia decomposition catalyst [6,7]. Here we show why the selection of the optimal ammonia decomposition catalyst is not just a matter of selecting the best ammonia synthesis catalyst. In fact, we show that the most active ammonia decomposition catalyst is always different from the optimal ammonia synthesis catalyst.

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## 2. Methods

Supported Fe, Co, Ni, Cu, and Ru catalysts were prepared by incipient wetness impregnation of $MgAl_2O_4$ spinel with aqueous solutions of the metal nitrates. The impregnated supports were dried at 393 K and calcined at 723 K for 2 h. Heating the catalysts to 773 K in $H_2$/He (1:1) for 2 h before activity measurements ensured reduction of the catalysts. The particle size distributions of the metal particles of the supported catalysts were determined by scanning transmission electron microscopy.

We prepared $Co_3Mo_3N$ by heating $CoMoO_4$ in flowing ammonia to 923 K for 8 h. X-ray powder diffraction showed complete conversion to $Co_3Mo_3N$ with an average crystal size of 490 Å (D400). Furthermore, the catalyst was heated in pure ammonia for 5 h at 923 K before the activity measurement.

Decomposition of ammonia was studied in an integral plug flow reactor with flow rates of 75–200 $\mathrm{ml\,min^{-1}}$ at STP and at temperatures varying from 923 to 573 K. Feed compositions of He/$NH_3$ (1:1), $H_2$/$NH_3$ (1:1), and pure $NH_3$ were used. A U-tube quartz reactor with an inner diameter of 4 mm was loaded with ca. 200 mg catalyst (particle size 150–300 µm), resulting in a bed height of approximately 18 mm for the supported catalysts and ca. 6 mm for $Co_3Mo_3N$. The composition of the exit gas was determined with a calibrated mass spectrometer.

## 3. Results and discussion

A model was recently developed that describes the trends for catalytic ammonia synthesis activity over transition-metal catalysts [8]. It gives the net ammonia synthesis turnover frequency, $(r_{\mathrm{syn}} - r_{\mathrm{decomp}})/n$, as a function of the dissociative nitrogen adsorption energy on the active sites, where $n$ is the number of active sites. The active sites are $B_5$-type sites corresponding to step sites on hexagonal close-packed surfaces [8–10]. The dissociative chemisorption energy determines the activity of a metal in ammonia synthesis because it determines both the stability of the main surface intermediates (N and $NH_x$) and the activation energy of the rate-determining step of $N_2$ dissociation, which are linearly correlated through the Brønsted–Evans–Polanyi relation [8]. The model is consistent with the principle of microscopic reversability and can therefore also be used to describe the trends for ammonia decomposition when the ammonia concentration is higher than the equilibrium value, i.e., $\beta > 1$.

In the top panel of Fig. 1 we show some of the trend predictions (volcano curves) of the model under both ammonia synthesis and ammonia decomposition conditions.

To determine whether the model truly decribes ammonia decomposition trends, we carried out the reaction over a series of supported metal and alloy ($Co_3Mo_3N$) catalysts. The catalysts are described in Table 1.

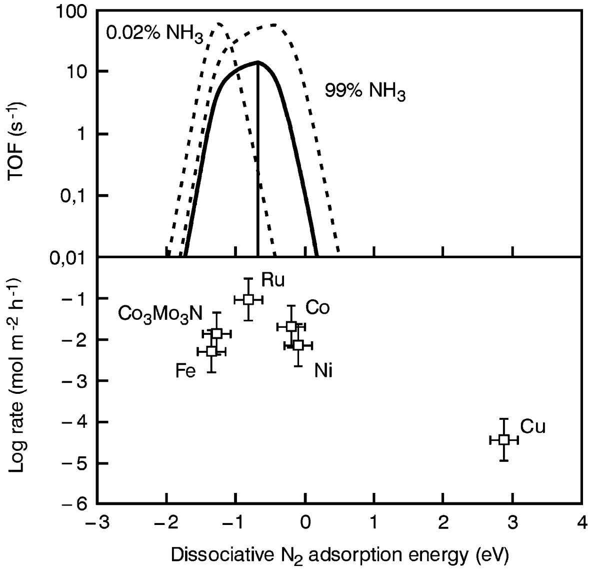

Fig. 1. Calculated turnover frequencies of ammonia synthesis/decomposition at 773 K, 1 bar, 3:1 $H_2/N_2$, and 0.02, 20 (solid line), and 99% $NH_3$ as a function of the reaction energy of dissociative $N_2$ adsorption. The vertical line gives the dissociative nitrogen binding energy of the optimal ammonia decomposition catalyst when the ammonia concentration is 20%. At these conditions the gas phase equilibrium $NH_3$ concentration is 0.13% (top). Experimental rates of ammonia decomposition over various catalysts at 773 K, 1 bar, 3:1 $H_2/N_2$, and 20% $NH_3$ (bottom).

Table 1
Metal loading and surface area of the catalysts

| Catalyst | Metal loading (wt%) | Average particle size (nm) | Active component surface area ($\mathrm{m^2\,g^{-1}}$) |
|---|---|---|---|
| Fe, $MgAl_2O_4$ | 4.6 | 13 | 2.9 |
| Co, $MgAl_2O_4$ | 5.2 | 20 | 1.7 |
| Ni, $MgAl_2O_4$ | 5.0 | 3 | 11 |
| Cu, $MgAl_2O_4$ | 5.4 | 500 | 0.067 |
| Ru, $MgAl_2O_4$ | 8.0 | 12 | 10 |
| $Co_3Mo_3N$ | – | 49[a] | 7[b] |

[a] Determined by X-ray powder diffraction (XRPD).
[b] Determined by $N_2$ physisorption (BET method).

To be able to compare the reaction rates over the catalysts under given reaction conditions, we need to model the experimental rates. For this purpose we found that a very simple kinetic model can describe the results obtained over all of the catalysts investigated. In the Langmuir–Hinselwood model it is assumed that desorption of nitrogen is the rate-determining step and $\theta_{\mathrm{N}} + \theta_{\mathrm{NH}_x} \cong 1$, where $x = 1$ or 2; $\theta_x$ is the surface coverage of species $x$. These assumptions are based on observations obtained from the trend model and in agreement with experimental observations [11].

As shown in Fig. 2, excellent descriptions of the observed rates are obtained. This suggests that the assumptions of the model are correct under the reaction conditions used.

In the bottom panel of Fig. 1, one set of results from the experimental findings is plotted as a function of the dissociative binding energy of nitrogen onto the active sites as

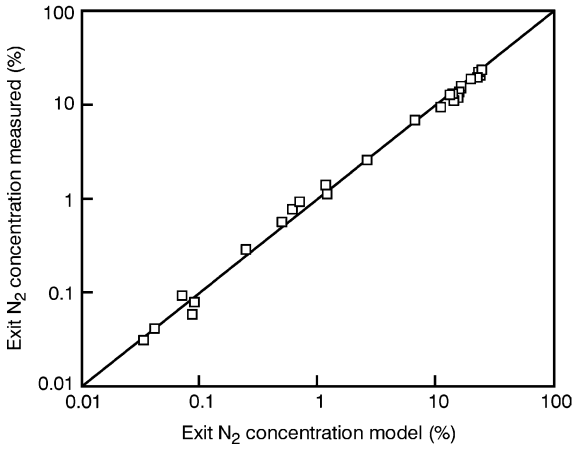

Fig. 2. The measured exit $N_2$ concentration plotted against the exit $N_2$ concentration described by the kinetic model using the ruthenium catalyst. Similar agreement between model and experiment are obtained with all catalysts.

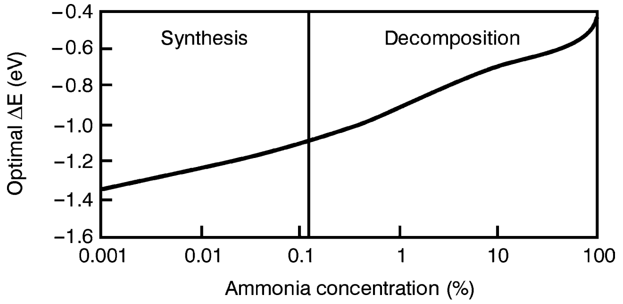

Fig. 3. Dissociative $N_2$ adsorption energy of optimal catalyst for ammonia synthesis/decomposition at 773 K, 1 bar and 3:1 $H_2/N_2$. Equilibrium corresponds to ca. 0.13% ammonia.

obtained from DFT calculations [12]. It is seen right away that the position of the experimentally observed volcano curve is in excellent agreement with that predicted from the trend model. The microkinetic model we use here describes ammonia synthesis over Ru very well if it is assumed that ca. 10% of the surface sites are active sites [9,13]. If this number is used to compare the absolute values in the two plots in Fig. 1, good agreement between predictions and experimental observations is also found.

Compared with the volcano curve for ammonia synthesis, the optimal catalyst for decomposition is one that binds nitrogen less strongly; that is, the maximum has moved away from iron and toward cobalt or nickel. As for the ammonia synthesis reaction, however, the position of the maximum of the volcano curve in ammonia decomposition is also highly dependent on the reaction conditions [14]. This is evident from the optimal catalyst curve developed for ammonia synthesis shown in Fig. 3, which is calculated for an isothermal reactor. We obtained the optimal catalyst curve simply by plotting the position of the maximum for volcano curves calculated at different ammonia concentrations, as illustrated in Fig. 1.

Thus, the optimal catalyst curve shows how the optimal nitrogen binding energy varies when the ammonia concentration is changed. Fig. 3 refers to both ammonia synthesis and ammonia decomposition. Interestingly, it is observed that the optimal ammonia synthesis catalyst is never the optimal ammonia decomposition catalyst. This does not mean that the principle of microscopic reversibility does not apply, but rather that the widely different reaction conditions in ammonia synthesis and ammonia decomposition result in very different optimal binding energies for the two reactions, except, of course, at equilibrium. Furthermore, it can be seen that in the optimal ammonia decomposition process it is necessary to grade the reactor with catalysts that have different nitrogen binding energies, as is also the case in the optimal ammonia synthesis process [14]. Finally, it is worth noting that the concept of interpolation in the Periodic Table, introduced to discover the new $Co_3Mo_3N$ catalyst in ammonia synthesis [15–17], can also be used to rationalize the activity of this new catalyst in ammonia decomposition. Here $Co_3Mo_3N$ is shown to have significant potential for ammonia decomposition, where the conventional promoted iron catalyst cannot be used because of the severe reaction conditions, where iron will form a bulk nitride. Particularly for use in small mobile units, where cost and size concerns are vital [18], the $Co_3Mo_3N$ catalyst appears to be the overall preferred catalyst because of its high density.

Thus, knowledge about the ammonia synthesis reaction can be used to accurately describe the ammonia decomposition reaction. Similarly, both the concept of optimal catalyst curves and the concept of interpolation in the Periodic Table are useful for both reactions. It is demonstrated that the optimal catalyst for ammonia decomposition is never the optimal catalyst for ammonia synthesis. Altogether, this suggests that the approach taken for ammonia synthesis could be useful for many other catalyst systems. This should lead to a more rational development of new and improved catalytic processes [16].

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