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A priori catalytic activity correlations: the difficult case of hydrogen production from ammonia

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The catalytic decomposition of ammonia has recently been proposed as a possible source of hydrogen for fuel cells. However, the ruthenium catalyst is costly. Although there exist several correlations for catalytic activity that suggest potentially useful alternatives, the particular candidates differ. The present work seeks to determine experimentally which, if any, of these correlations correctly predicts suitable substitutes. The experiments examine 13 different metallic catalysts from numerous places within the Periodic Table, and show that the activity varies in the order Ru > Ni > Rh > Co > Ir > Fe ≫ Pt > Cr > Pd > Cu ≫ Te, Se, Pb. The results suggest that nitrogen desorption limits the rate on Fe, Co, and Ni, whereas N–H bond scission limits the rate on other metals such as Rh, Ir, Pd, Pt, and Cu. Conventional single-parameter correlations of activity generally fail to predict the results because the rate-determining step changes across the data set.

KEY WORDS: hydrogen from ammonia; decomposition of ammonia.

1. Introduction

The catalytic decomposition of ammonia has recently been proposed as a possible source of hydrogen for fuel cells [1–3]. Ammonia is readily available, has a high energy content, exhibits a narrow explosion limit, and decomposes relatively easily with no need for added steam or oxygen. These advantages make ammonia particularly suited as a hydrogen carrier for portable power applications.

However, one disadvantage of ammonia is the cost of the catalyst. The kinetics of ammonia decomposition has been studied on several metals [1,4–8], including ruthenium, iridium platinum and nickel. Of these metals, ruthenium exhibits the most activity by a significant margin. Ruthenium is unfortunately very expensive. Currently, the experimental literature is not sufficiently extensive to determine whether there exist less expensive metals that can adequately substitute for ruthenium.

Common models for catalytic reactivity and their associated rate correlations point to several candidates, however. For example, one model predicts that the rate should increase with the energy of the center of the d-band relative to the Fermi level [9,10,11], suggesting particularly high activity for iron and chromium. Another model predicts that the rate should correlate with the heat of formation of the metal oxide [12–16], suggesting particularly high activity for tellurium, selenium and lead. Other models focus on the heat of chemisorption of ammonia or nitrogen [17–20], or the percent d-character of metal bonding [21,22]. Correlations based upon these models, respectively, predict high activity for cobalt and nickel, or for palladium.

Although all these correlations suggest potentially useful alternatives to ruthenium for ammonia decomposition, the particular candidates differ. The present work seeks to determine experimentally which, if any, of these correlations correctly predicts suitable substitutes for ruthenium. The experiments examine 13 different metallic catalysts from numerous places within the Periodic Table in order to subject the various correlations to stringent testing and to maximize the chances of finding an inexpensive substitute for ruthenium. The metals include Group VIII elements typically used as catalysts, as well as other metals possessing related chemical properties.

2. Experimental

Experiments employed metals supported on pellets of activated alumina. Several catalysts were obtained from a commercial source (Alfa Aesar), including those containing Pd, Pt, Ir, Rh, and Ru. The remaining catalysts were made using conventional wet impregnation into blank pellets (Alfa Aesar) using metal nitrates or chlorides dissolved in water or acetone. The catalyst used in each experiment typically contained 2–10 mg of metal. Prior to rate measurements, all catalysts were oxidized in flowing air at 550 °C for 8 h and were subsequently reduced in flowing hydrogen at 550 °C for 2 h.

The reaction apparatus consisted of a quartz tube (14 in. long, 0.25 in. inside diameter) heated by a

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temperature-controlled tube furnace. Several blank alumina pellets were placed upstream of the reaction zone to act as a gas preheater. Species concentrations in the effluent were monitored by a differentially pumped quadrupole mass spectrometer (Extrel C-50). The base pressure of the sampling chamber was roughly 10^{-9} Torr, and measurement pressures were typically near 10^{-7} Torr. Mass spectrometer calibration was accomplished by passing known mixtures of ammonia, hydrogen, and nitrogen into the sampling chamber. The reactant stream consisted of technical grade (99.99%) anhydrous ammonia at atmospheric pressure, whose flow rate was controlled using a calibrated mass flow controller. Control experiments showed that the reactor system induced no conversion in the absence of metal catalyst.

Rates were measured under differential conversion conditions (5%) at a temperature of 580 °C. The catalysts containing Te, Se and Pb exhibited no measurable conversion even at the lowest flowrates that were practical in the apparatus. Thus, only an upper bound on the rate could be established.

Normalization of the rates in terms of turnover frequencies (TOF) required measurements of the degree of catalyst dispersion, which was determined for each metal using either pulse chemisorption of CO or oxidation with N_2O. The chemisorption measurements were performed using a commercial apparatus (Micromeritics Pulse ChemiSorb 2705).

3. Results and discussion

Table 1 summarizes the measured turnover frequencies. Ruthenium is the most active metal. For convenient comparison, table 1 shows the TOF both in raw form and in terms of a ratio normalized to ruthenium. Nickel has an activity that is broadly comparable to ruthenium (~40% lower), but all the other metals examined have activities that lie a factor of three or more lower than ruthenium in agreement with previous measurements [1].

Table 1
Measured TOF for ammonia decomposition over several supported metal catalysts

Catalyst	Dispersion (%)	TOF (s^{-1})	TOF/Ru TOF
0.5 wt% Ru/Al_2O_3	48	6.85	1
1.0 wt% Ni/Al_2O_3	0.9	4.21	0.61
0.5 wt% Rh/Al_2O_3	65	2.26	0.33
1.0 wt% Co/Al_2O_3	2.3	1.33	0.19
1.0 wt% Ir/Al_2O_3	47	0.786	0.11
1.0 wt% Fe/Al_2O_3	0.7	0.327	0.048
1.0 wt% Pt/Al_2O_3	31	0.0226	0.0033
1.0 wt% Cr/Al_2O_3	1.9	0.0220	0.0032
0.5 wt% Pd/Al_2O_3	39	0.0194	0.0028
1.0 wt% Cu/Al_2O_3	5.1	0.0130	0.0019
1.0 wt% Te/Al_2O_3	4.2	<0.0056[a]	<0.00082
1.0 wt% Se/Al_2O_3	2.9	<0.0044[a]	<0.00065
1.0 wt% Pb/Al_2O_3	16	<0.0024[a]	<0.00035

[a] Maximum possible rate, actual rate is below the mass spectrometer detection limit.

Of the correlations discussed earlier, the model focusing on the chemisorption heat of ammonia or nitrogen comes closest to accuracy in predicting a substitute for ruthenium. That model suggests that nickel or cobalt should have particularly high activity. The activity of nickel lies within 40% of ruthenium, and cobalt lies within a factor of five. However, that model fails to predict the higher activity of rhodium (within a factor of three of ruthenium) compared to cobalt.

A more detailed examination of the data shows that the inadequacies of this and other models run deeper, however. Ammonia decomposition into hydrogen has a simple mechanism that has been mapped out extensively by computations [9,10,17,18,23,24]. The mechanism has the following steps:

$$NH_3 \leftrightarrow NH_{3,ad} \quad (1)$$

$$NH_{3,ad} \rightarrow NH_{2,ad} + H_{ad} \quad (2)$$

$$NH_{2,ad} + H_{ad} \rightarrow NH_{ad} + 2H_{ad} \quad (3)$$

$$NH_{ad} + 2H_{ad} \rightarrow N_{ad} + 3H_{ad} \quad (4)$$

$$2H_{ad} \rightarrow H_2 \quad (5)$$

$$2N_{ad} \rightarrow N_2 \quad (6)$$

These steps constitute the exact reverse of ammonia formation from hydrogen and nitrogen [25], so it is reasonable to suppose that catalysts known to be especially active for ammonia formation would also be active for ammonia decomposition. However, comparison of the data of table 1 with formation data summarized in [25] shows that this correspondence does not hold. In particular, iron shows high activity for formation but not for decomposition. It is important to note, however, that the present experiments were conducted under conditions very different from those that prevail in a typical ammonia synthesis reactor. In particular, the present experiments employed much lower pressures and much higher temperatures. The rate-determining step may therefore change, and with it the most effective catalyst.

In ammonia synthesis, nitrogen adsorption is generally rate-determining [17,25]. Exact correspondence with ammonia decomposition would suggest that the reverse of this step limits the rate – that is, nitrogen desorption. Under this premise, the rates measured here for various metals should scale with the corresponding rates of nitrogen desorption. However, figure 1 shows that such scaling is not observed. Desorption rates in figure 1 were estimated using the Blowers–Masel equation [26,27,30], which relates reaction activation barriers to the heat of reaction and intrinsic activation energies. To calculate the rate of N_2 desorption for each metal, the heat of

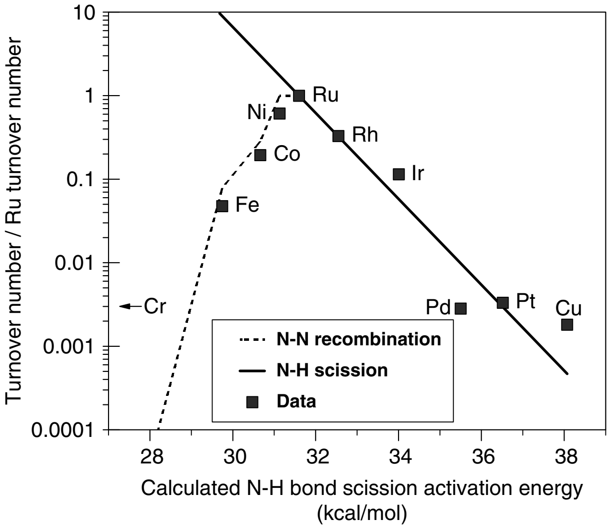

Figure 1. A correlation between the rate of ammonia decomposition on several metals and the relative rate of N–H bond scission, and N–N recombination as estimated from the Blowers–Masel correlation.

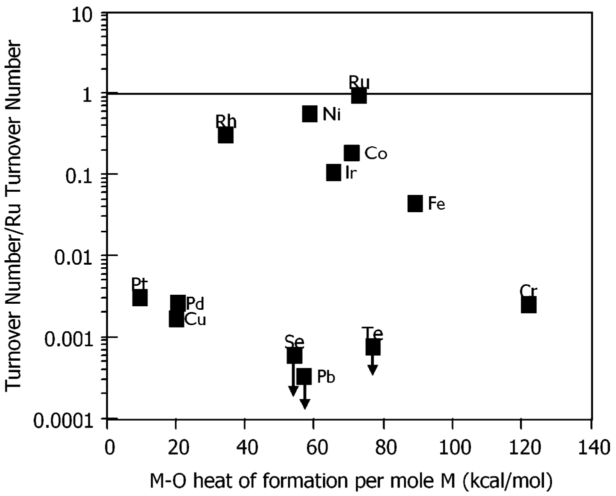

Figure 3. A correlation between the rate of ammonia decomposition on several metals and the metal–oxygen bond strength per mole of metal.

reaction was calculated using the metal–nitrogen bond energies shown on the ordinate. The equation was employed with an intrinsic activation barrier E_a^0 of 28 kcal/mol, the experimental activation barrier for N_2 desorption from platinum [28]. Figure 1 shows that Ru, Ni, Co, Fe and Cr follow the predicted increase in decomposition rate with nitrogen desorption rate. However, the data for Rh, Ir, Pt, Pd and Cu follow the opposite trend, suggesting that the rate-determining step has changed.

Figure 1 also shows the trend expected with a different rate-determining step: the scission of adsorbed N–H [equation (4)]. To calculate the rate of N–H bond scission for each metal, the heat of reaction was calculated using the metal–nitrogen bond energies shown on the ordinate in addition to metal–hydrogen bond energy. This scission rate was estimated by the Blowers–Masel [26,27] equation using an intrinsic activation barrier of 35 kcal/mol [29]. This choice of rate-determining step matches the quite well for Ru, Rh, Ir, Pt, Pd and Cu. This choice also explains why Pb, Se, and Te are inactive, since scission is symmetry forbidden with $E_a^0 > 100$ kcal/mol [29]. Pb, Se, and Te are therefore not included in figure 1.

Notice that the rate of N–H bond scission increases as the energy of the nitrogen surface bond increases, while the rate of N_2 desorption decreases as the energy of the nitrogen surface bond increases. This

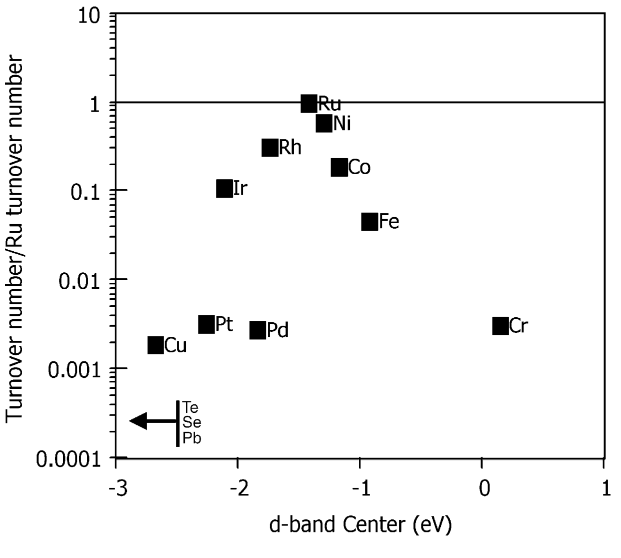

Figure 2. A correlation between the rate of ammonia decomposition on several metals and the energy of the center of the d-band.

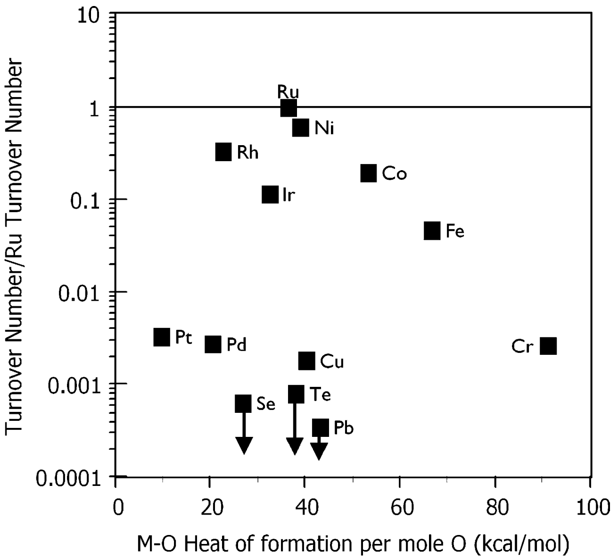

Figure 4. A correlation between the rate of ammonia decomposition on several metals and the metal–oxygen bond strength per mole of oxygen.

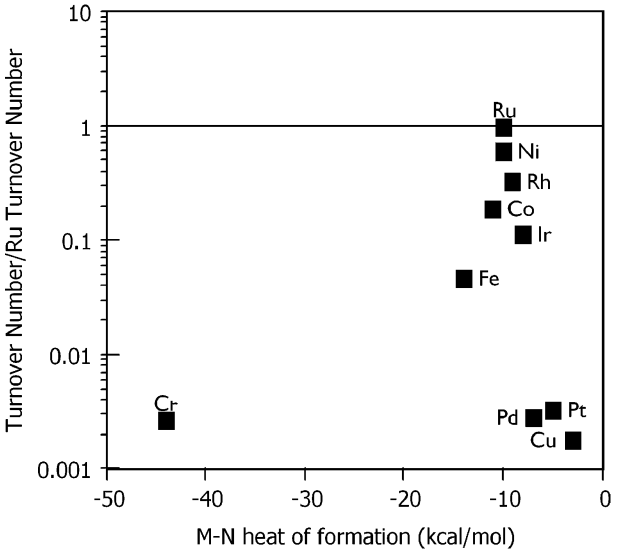

Figure 5. A correlation between the rate of ammonia decomposition on several metals and the metal–nitrogen bond strength.

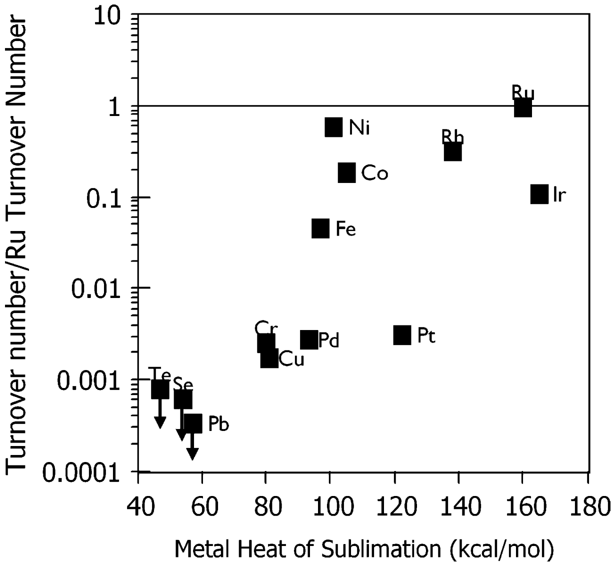

Figure 6. A correlation between the rate of ammonia decomposition on several metals and the heat of sublimation of the metal.

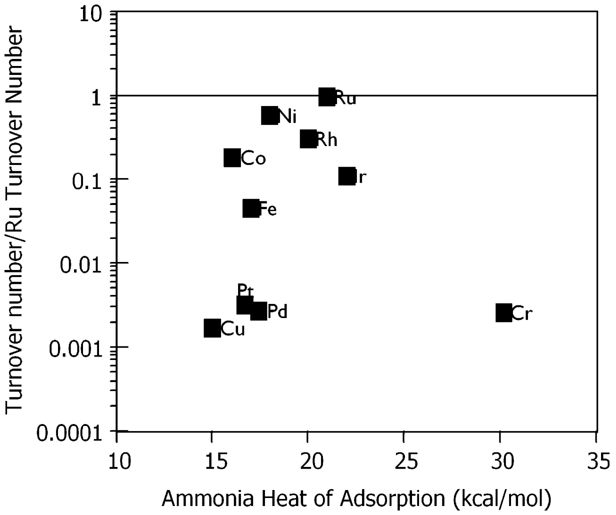

Figure 7. A correlation between the rate of ammonia decomposition on several metals and the heat of adsorption of ammonia on the metal.

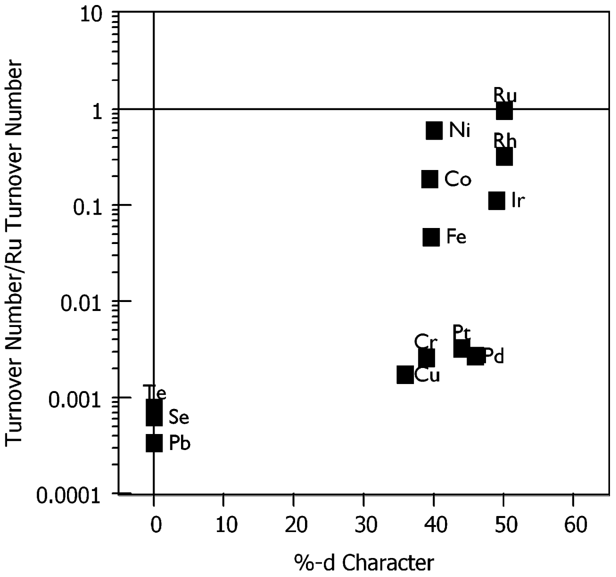

Figure 8. A correlation between the rate of ammonia decomposition on several metals and the percent d-character of the metal.

occurs because an N-surface bond is formed during N–H bond scission, while an N-surface bond breaks when N desorbs.

In aggregate, the results of figure 1 suggest that rate-determining step for ammonia decomposition under the conditions examined here depends upon the activity of the metal with regard to either nitrogen desorption or N–H bond scission. These two steps are influenced quite differently by the chemical properties of the metal. For example, nitrogen desorption is enhanced by moderate nitrogen–metal bond strengths but inhibited by very strong bonding to nitrogen, such as that exhibited by chromium. By contrast, N–H bond scission is inhibited by a center-energy for the d-band that is either too high or too low.

Thus, it should be expected that single-parameter correlations of catalytic activity perform poorly for ammonia decomposition. Indeed, analysis of the present data set in terms of such correlations bears out this difficulty. Figures 2–8 show examples, with table 2 listing the relevant correlation parameters for each metal. Pb, Se, and Te catalysts are not included in figures 5 and 7 due to the lack of data for the nitrogen binding energy and ammonia heat of adsorption, respectively, for each of these metals. All the correlations are single-parameter, focusing upon energy of the d-band center [11–13] (figure 2), heat of formation of the oxide per mole of oxygen (figure 3) or metal (figure 4) [12–16], heat of adsorption of nitrogen (figure 5) [9,10,17,18,23,24], heat of sublimation of the metal

Table 2
A comparison of some of the physical properties of the catalysts used in the work here

Metal	d-band center (eV) [16]	$\Delta H_{f,M-O}$[a] (kcal/mol)	$\Delta H_{f,\ M-O}$[b] (kcal/mol)	$\Delta H_{f,\ M-N}$ (kcal/mol)	%-d character	$\Delta H_{sublimation}$ metal (kcal/mol)	NH_3 ΔH_{ads} (kcal/mol)
Ru	−1.41	72.8	36.4	10	50	160	21
Ni	−1.29	58.5	39	10	40	101	18
Rh	−1.73	34.2	22.8	−9	50	138	20
Co	−1.17	70.9	53.2	−11	39.5	105	16
Ir	−2.11	65.5	32.7	−8	49	165	22
Fe	−0.92	89	66.8	−12	39.7	97	17
Pt	−2.25	9.7	9.7	−5	44	122	16.7
Cr	+0.16	122	91.4	−44	39	80	30.2
Pd	−1.83	20.4	20.4	−7	46	93	17.4
Cu	−2.67	20.1	40.3	−3	36	81	15
Te	−40.4	77	38	–	0	47	–
Se	−54.6	54	27	–	0	54	–
Pb	−18.1	57	43	–	0	57	–

[a] Metal-oxide bond strength per mole of metal (Tanaka–Tamaru).
[b] Metal-oxide bond strength per mole of oxide (Sachtler–Fahrenfort).

(figure 6) [12], heat of adsorption of ammonia (figure 7) [19,20], and percent d character of the metal (figure 8) [21,22]. In no case is the correlation fit satisfactory.

Note that ruthenium and nickel are located near the convergence of the two plots in figure 1. Thus, it is not clear which step [equation (4) or (6)] limits the rate. However, it is clear that these two metals lie at an optimum, where no chemical property of the metal slows the rate-determining step to a great extent. Unfortunately, *a priori* prediction of the position of such optima is difficult when the rate-determining step can change because the tradeoff between the enhancements and inhibitions of various chemical properties on each possible step must be known quantitatively.

These results illustrate the drawbacks of using a single parameter to predict reactivity. Broadening the range of metals considered leads to a higher risk that the rate-determining step changes across the data set. Different rate determining steps can behave quite differently in response to changes in the various chemical properties of the metal. Generally, such models work only under narrow circumstances, and have limited utility in predicting the activities of metals outside the range in which the model has been verified by experiments.

4. Conclusions

The results presented here highlight significant difficulties in trying to make *a priori* predictions of catalytic behavior. Correlations of activity typically make the tacit assumption that for a given reaction, a single rate-determining step governs the behavior over a broad range of metals. The present example of ammonia decomposition offers a counterexample where the rate-determining step almost certainly changes.

Unfortunately, the existence and location of such changes in the Periodic Table are very difficult to ascertain ahead of time. Broadening the range of metals considered leads to a higher risk that the rate-determining step changes across a data set, so that single-parameter correlations have correspondingly lower utility for prediction.

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