

# Heterogeneous Catalytic Oxidation of Ammonia by Various Transition Metals

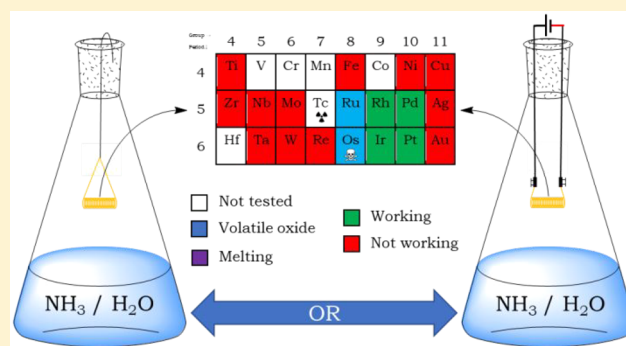
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## Supporting Information

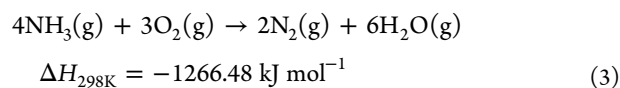
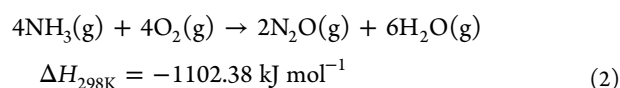
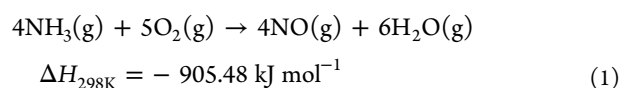
**ABSTRACT:** A well-known demonstration is adapted to simplify the illustration of heterogeneous catalytic oxidation of ammonia. Various metal catalyst wires are placed above the liquid level in a flask containing concentrated ammonia. After brief preheating, some metal wires continue to glow, providing visual evidence of an overall exothermic reaction taking place at the catalytic surface. Thermal heating by a butane flame prior to insertion and *in situ* resistive heating using a power supply yield identical results. Active catalysts are the group 9 and 10 elements Rh, Ir, Pd, and Pt. Besides the illustration of the Sabatier principle, the effect of the ammonia-to-oxygen ratio can also be visualized, and active metals vary in the production of a grayish smoke. These observations provide a starting point to discuss catalytic selectivity, a topic of great relevance to industrial catalytic oxidation of ammonia.

**KEYWORDS:** High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Physical Chemistry, Catalysis, Metals, Periodicity/Periodic Table



A visually attractive lecture demonstration of heterogeneous catalysis is the “exploding flask” experiment.<sup>1–6</sup> A glowing wire of an appropriate transition metal is placed in a flask containing a layer of methanol. The wire continues to glow, providing evidence of an exothermic reaction occurring at the catalytic surface. While many combinations of transition metals and alcohols may be used,<sup>5</sup> recurrent explosions are only observed for the combination of Pt and methanol. This was recently attributed to the efficient dehydrogenation of methanol with recombinative hydrogen desorption leading to a buildup of an explosive hydrogen–oxygen mixture in the flask.<sup>6</sup>

Whereas the “exploding flask” demonstration illustrates heterogeneous catalysis and provides a means to introduce catalytic activity, the oxidation of ammonia is a better starting point to discuss catalytic selectivity. As mentioned in previous reports of demonstration experiments on this topic,<sup>7–15</sup> the following reaction equations describe the possible chemical conversions associated with the oxidation of ammonia:



Reaction 1 describes the first step of the Ostwald process for the production of nitric acid (HNO<sub>3</sub>), the main raw material for fertilizers.<sup>16,17</sup> The oxidation toward nitrous oxide (N<sub>2</sub>O, laughing-gas) is described by reaction 2.<sup>18</sup> Nitrous oxide has, among other uses, medical uses for its anesthetic and pain reducing effects.<sup>19,20</sup> Oxidation of ammonia toward nitrogen gas (N<sub>2</sub>) in reaction 3 is used as an environmentally friendly method to reduce ammonia emissions.<sup>21</sup> The stoichiometry in these reactions suggests that variations in the ammonia-to-oxygen ratio may be used to control product composition. However, this argument neglects that catalytic materials may show a preference for a particular product resulting from, e.g., the stability of particular intermediates, i.e., catalytic selectivity.

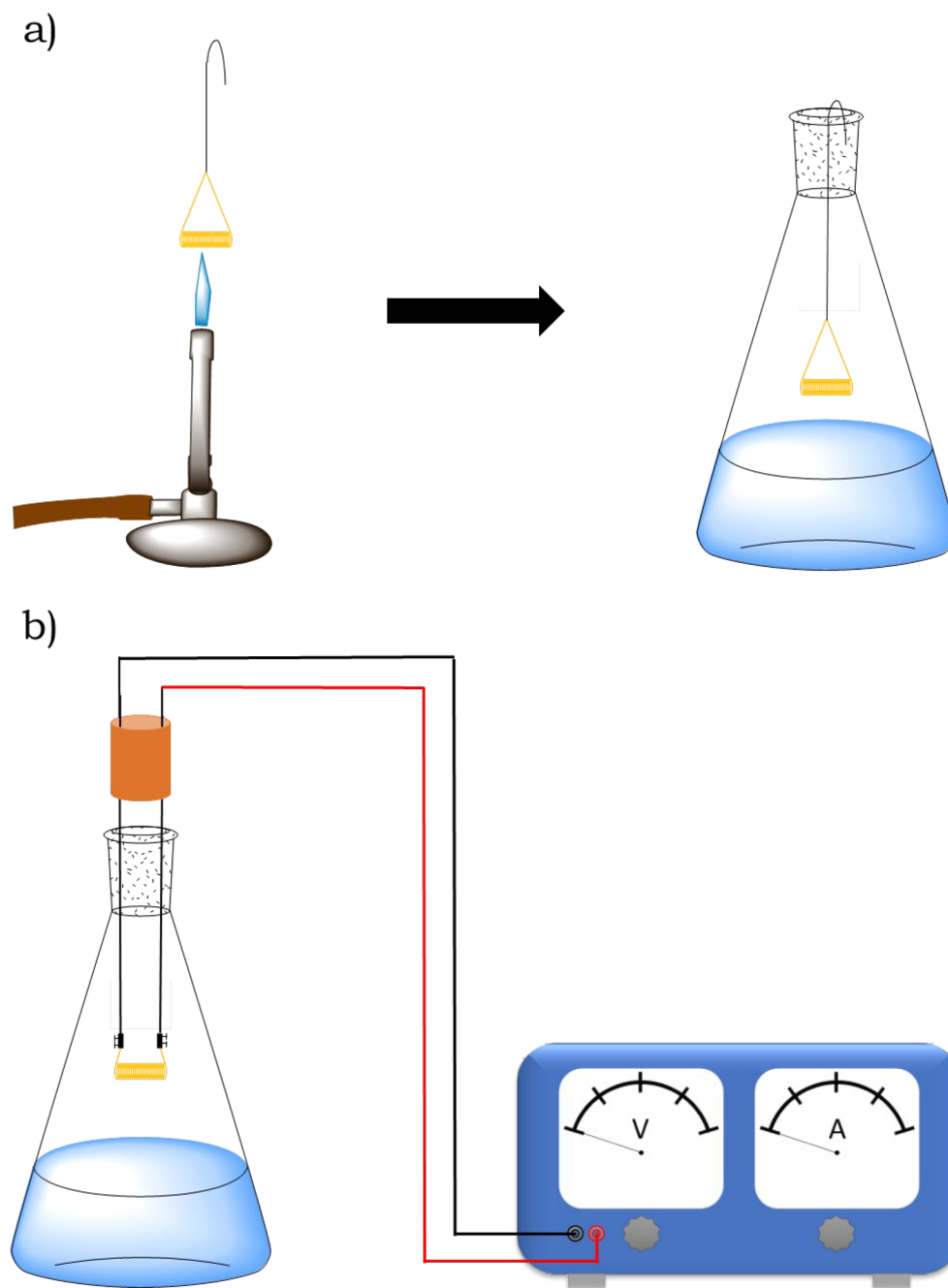
Most of the described demonstration experiments illustrating ammonia oxidation<sup>7–15</sup> require nonstandard glassware, make use of a closed system with the risk of overpressurizing and explosion, or require the use of a catalyst that is suspected to be carcinogenic.<sup>7–9,11,14,15</sup> This makes many descriptions difficult or unsuitable for classroom demonstrations. All reports have in common that they include only a single catalyst material. The added value of these experiments is thus limited, and general periodic trends in heterogeneous catalysis cannot be deduced.

Here, we report an adaptation of the “exploding flask” demonstration to illustrate catalytic ammonia oxidation. Using

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**Figure 1.** Schematic representation of the setups for (a) thermal heating by a butane flame prior to insertion and (b) *in situ* resistive heating using a power supply of the considered metal catalysts.

a flame or a power supply, we heat various transition metal catalysts in a standardized setup, resulting in a remarkably practical demonstration experiment that can be used to initiate discussion on many aspects of heterogeneous catalysis. The demonstration is complementary to heterogeneous catalytic oxidation of alcohols, reported by our group earlier in this *Journal*,<sup>5,6</sup> and well-suited to expand upon the topic.

#### ■ HAZARDS

The ammonia solution causes severe skin burns and eye damage when in direct contact. The solution should be handled with care wearing protective gloves, protective clothing, and eye protection. Its vapors can cause respiratory irritation and are toxic if inhaled. An appropriate distance

between any heating device and the setup should be maintained when preheating the catalyst.

Possible products, of which small amounts will escape from the setup, are the harmful nitrogen oxides and harmless nitrogen gas. On the basis of ref 15, the maximum amount of nitrogen oxides formed using this demonstration is 19 mL at 1 atm. When discharged into 1 m<sup>3</sup>, the concentration is 19 ppm. Only exposure to concentrations >100 ppm are dangerous, and it is not strictly necessary to perform this experiment in a fume hood. However, concentrations near the setup may be higher, and good ventilation is recommended. Highly flammable materials should be kept at an appropriate distance from the experimental setup since gaseous products are oxidizers.

| Group →<br>Period ↓ | 4  | 5  | 6  | 7       | 8       | 9  | 10 | 11 |
|---------------------|----|----|----|---------|---------|----|----|----|
| 4                   | Ti | V  | Cr | Mn      | Fe      | Co | Ni | Cu |
| 5                   | Zr | Nb | Mo | Tc<br>☢ | Ru      | Rh | Pd | Ag |
| 6                   | Hf | Ta | W  | Re      | Os<br>☠ | Ir | Pt | Au |

**Figure 2.** Overview of scaled reactivity of d-block metals toward the room temperature oxidation of ammonia: red = the metal stops glowing immediately, green = the metal keeps on glowing continuously, blue = volatile oxide, and white = not tested.

Use of a power supply may cause shocks and burns if in contact with live parts, fires as a result of defects in cabling, or ignition of an explosive atmosphere. In order to prevent a short circuit, it is recommended that one work in a moisture-free environment, increase the current slowly, and only use certified cables and connectors.

Osmium and ruthenium are not suitable to use in an oxygen-rich atmosphere at high temperatures due to the toxicity of their oxides.

## EXPERIMENTAL SECTION

Figure 1 schematically shows our standardized apparatus. A 500 mL Erlenmeyer flask is charged with 75 mL of a concentrated ammonia solution available in our laboratory (25 vol % in water, ACS, J.T. Baker). Metal catalysts consisting of about 2.0 mm diameter spirals are made from 4–10 cm long wires with a diameter of 100–300  $\mu\text{m}$ . We used stock materials from European vendors, e.g., MRC Materials Research Corporation (Les Pavillons sous Bois, France) and Platecxis-Drijfhout (Purmerend, The Netherlands). The same may also be purchased from, among others, Sigma-Aldrich. The catalysts are preheated using a blue butane flame and placed approximately 5 cm above the liquid level (Figure 1a).

The time between preheating and starting the experiment is kept short but may be eliminated by heating using a power supply. We connect two vertical insulated aluminum rods, which are held in place by a rubber septum, to the catalyst with metal screw terminals allowing for easy replacement of the catalyst (Figure 1b). The standing clamp holding the septum well above the orifice of the flask is not shown for reasons of clarity. The wire is gently heated using a dc power supply (BST PSM 2/5A) until the wire starts to glow brightly. Hereafter, the power supply is switched off. The same set of metal catalysts are tested using both setups. The ammonia solution was at room temperature in all experiments.

## RESULTS AND DISCUSSION

To investigate the catalytic reactivity of transition metals toward ammonia oxidation, all metals available as wires in our laboratory were tested. All metal wires glow upon preheating with a blue butane flame in air and keep glowing for the time period of seconds in which the catalyst is placed in the

Erlenmeyer flask (Figure 1a). In the other set of experiments, the majority of the metal catalysts start glowing when a current is applied to the catalyst wire (Figure 1b). An overview of the applied voltage and observed current for the active catalysts can be found in the Supporting Information. However, upon slowly increasing the current, group 11 metals melted before starting to glow, and the available iridium wire did not glow, which we attribute to its low resistivity.

Results for the metals as catalysts for ammonia oxidation are shown in Figure 2. Catalytic activity was determined by the color of the glowing metal wire, which gives a rough indication of the temperature. A metal wire hanging over the 25 vol % ammonia solution was considered catalytically active if it continued to glow visibly for an extended period of time after the heat source was removed. When the heat source was removed, the temperature of active catalyst wires generally decreased prior to stabilization. Now and then, a decrease was followed by an increase. As can be concluded from Figure 2 and the videos in the Supporting Information, the physical behavior of the four active catalysts is independent of the way it is heated. The same experiments carried out using household ammonia were unsuccessful, likely as a consequence of the lower ammonia concentration (1–5 vol % in water) and, thus, lower ammonia partial pressure.

Notable other observations are the following: (1) After removal of active catalyst wires from the flask and letting them cool, they appear the same as prior to the experiment. (2) During the catalytic oxidation of ammonia with Rh and Pt, evolution of a grayish smoke is observed. This gas production is not observed for Ir and Pd. (3) During the catalytic oxidation using a platinum mesh catalyst, the bottom part of the mesh glows brighter than the top part.

From Figure 2 it can be seen that the active metals are solely found in groups 9 and 10 of periods 5 and 6. Although results are in accordance with reactivity for transition-metal-based molecular systems,<sup>22</sup> others have reported metallic Cu as an active metal in the ammonia oxidation.<sup>8,10,13</sup> This difference is likely attributable to experimental design, with others using a mixture of pure ammonia gas and oxygen instead of ammonia vapor in air. The higher partial pressures may make less reactive metals maintain a higher catalyst temperature by increasing reaction rates.

The observations and results of this demonstration, in particular when multiple transition metal catalytic wires are used, illustrate various aspects of heterogeneous catalysis. We outline an option with increasing complexity of concepts and learning goals.

First, active metal wires appearing identical before and after the demonstration suggest that the wires themselves do not chemically change from the experiment. In addition, repeatedly performing an oxidation reaction with the same catalysts yields identical results further supporting this conclusion. From the continued glowing upon suspension of the wire over the ammonia solution, students should arrive at the conclusion that the required heat must originate from an exothermic chemical reaction occurring at the catalyst's surface only. When the wire is not suspended over ammonia, there is an absence of the glowing, so it seems likely that the heat results from oxidation of ammonia. The results being independent of the method of preheating suggest that only temperature is important to get the self-sustaining reaction started.

Second, even when using a subset of transition metals, the results can be used to qualitatively illustrate the Sabatier principle.<sup>23</sup> This principle explains why *catalytic activity* is governed by the position of the element in the periodic table.<sup>24</sup> Early transition metals often interact strongly with reactant(s), intermediate(s), and/or product(s). The catalytic surface is quickly deactivated by poisoning as intermediates or products do not desorb from the surface, blocking all catalytically active sites. Late transition metals, on the other hand, have weak interactions with reactant(s). If reactants do not dissociate on the catalytic surface, the product is never formed. Between these two extremes, the catalyst performs optimally. Plotting the reaction rate versus the elements' group results accordingly in a so-called volcano plot. At the volcano's peak, the optimal balance between reactivity toward the reactants and the ability to have products leave the surface is achieved. If the similar methanol catalytic oxidation demonstration<sup>5,6</sup> was used prior to ammonia oxidation demonstration, it may be noted that (1) some metals are active in both oxidation reactions and (2) ammonia oxidation is much more sensitive to the choice of metal catalyst. The *catalytic activity* being "just right" varies with the chemical reaction of interest.

Third, the observation of a temperature gradient on a small piece of Pt catalyst mesh illustrates the effect of variation in the ammonia-to-oxygen stoichiometry. Here, students may be introduced to the industrial relevance of ammonia oxidation and the chemical reactions leading to different products as shown in reactions 1–3. Critical students may suggest that stoichiometry may favor formation of one product above the other, which is indeed one of the possible strategies for selective ammonia oxidation.<sup>25</sup>

Finally, students may be introduced to *catalytic selectivity* by noting that some active metals produced a grayish smoke while others did not. An example of Pt showing this gas evolution is presented in the Supporting Information videos. They may be asked to consider the origin of this observation in relation to the chemical reactions. Even without introducing potential subsequent reactions, e.g., NO oxidation to NO<sub>2</sub> by excess O<sub>2</sub> and formation of N<sub>2</sub>O<sub>4</sub> from NO<sub>2</sub>, it may be concluded that different active metals produce gaseous products to varying degrees, i.e., *chemical selectivity*. We have performed detailed research on this demonstration using infrared spectroscopy and mass spectrometry using a controlled environment and gas flow consisting of O<sub>2</sub>/Ar mixtures, similar to our previous work

on the oxidation of methanol.<sup>5</sup> Results confirm product selectivity toward N<sub>2</sub>, N<sub>2</sub>O, NO, and NO<sub>2</sub> that depends on catalyst material and gas flow composition.

## CONCLUSION

The reactivity of transition metals toward the heterogeneous catalyzed oxidation of ammonia was systematically examined using two different ways of preheating the catalyst in a standardized setup available to any laboratory. We have exemplified how observations can be used to progress along a series of concepts of increasing complexity that are central to heterogeneous catalysis. The same equipment may be used for the "exploding flask" demonstration, which is visually more attractive, and may be used to spark students' initial interest. The use of the same simple equipment also lowers investment cost and removes potential hurdles to students' understanding and learning.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00351.

Thermodynamic data, experimental parameters, physical properties, and H- and P-phases of reactants and products (PDF, DOCX)

Performance of experiments using Cu wire by preheating with thermal heat (MP4)

Performance of experiments using Ir wire by preheating with thermal heat (MP4)

Performance of experiments using Pd wire by preheating with thermal heat (MP4)

Performance of experiments using Pt mesh by preheating with thermal heat (MP4)

Performance of experiments using Pt wire by preheating with thermal heat (MP4)

Performance of experiments using Rh wire by preheating with thermal heat (MP4)

Performance of experiments using Pd wire by preheating with resistive heat (MP4)

Performance of experiments using Pt wire by preheating with resistive heat (MP4)

Performance of experiments using Rh wire by preheating with resistive heat (MP4)

Performance of experiments using Pt wire showing smoke formation (MP4)

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### Notes

The authors declare no competing financial interest.

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