Heterogeneous Catalytic Oxidation of Simple Alcohols by Transition Metals

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Heterogeneous Catalytic Oxidation of Simple Alcohols by Transition Metals

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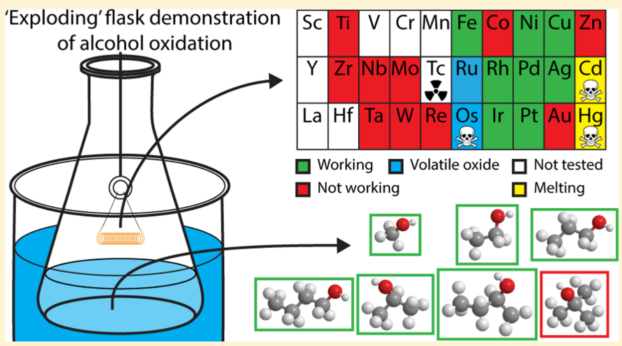
ABSTRACT: The "exploding" flask demonstration presents a well-known illustration of heterogeneous catalyzed methanol oxidation. We find that for the same vapor pressure, the demonstration also works for all primary and secondary alcohols up to butanol but not for a tertiary alcohol. Also, we show that the demonstration works for a large range of transition metal catalysts. Hence, this demonstration, which is often applied for the repetitive explosions when methanol is used, may also be used to argue the requirement of initial dehydrogenation of the alcohol to an aldehyde in the catalytic reaction mechanism to support the general insensitivity to reactant molecules in heterogeneous catalysis in contrast to biological catalysis and to provide proof for activity trends as often depicted by volcano plots.



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The repeating "exploding" flask experiment is a rare example of a visually attractive demonstration of heterogeneous catalysis.[1−4] In this experiment, a preheated catalyst, typically Pt or Cu, is put above the liquid surface of methanol in an Erlenmeyer flask. Due to the exothermicity of the overall reaction, the temperature of the wire will increase. If the conditions are optimal, the gas mixture will explode once the temperature reaches its maximum. During the explosion, gases are pushed out of the flask, the temperature of the catalyst decreases, and the cycle starts again. Formaldehyde is reported to be detected by its pungent smell and, therefore, suggested to be one of the products of this reaction. From this observation, it was concluded that the key reaction is the decomposition of methanol by

$$H_3C{-}OH(g) \rightarrow H_2C{=}O(g) + H_2(g) \quad (1)$$

However, as this reaction is endothermic, it should be accompanied by the oxidation of the produced hydrogen gas by

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad (2)$$

which is strongly exothermic. The explosion is ascribed to the spontaneous combustion of methanol due to the increased temperature of the catalyst.[1] However, this seems to be in contradiction to the absence of explosions when the demonstration is performed in a beaker instead of an Erlenmeyer flask.[2] Indeed, as studied in our group, it seems more plausible that the explosion is due to an increase in the background pressure of H_2.[5]

Heterogeneous catalysts are, compared to biocatalysts and homogeneous catalysts, typically not extremely selective toward different reactant molecules. Thus, it might be expected that a wide variety of alcohols and d-block metals could be used for this demonstration as described in reaction 3.

$$H_{2n+1}C_nOH(g) \rightarrow H_{2n}C_nO(g) + H_2(g) \quad (3)$$

However, the descriptions available from the literature are rather limited and not unambiguous. De Gruijter uses a copper wire catalyst for his experiments.[3] Battino et al. tested Pt, Pd, Ni, Ni/Cu, and silver for methanol, ethanol, and 1-propanol with varying results.[1] However, a significant part of these options were found to work "sometimes". Finally, Weimer claims that Cu, Al, Fe, and Ni remain inert to the reaction, which is in contradiction with both De Gruijter and Battino et al.[1,3,4] However, it should be noted that the experimental conditions used by the different authors are not all very well-defined.

In this study, we test a wide variety of d-block metals and simple $C_1{-}C_4$ alcohols using a standardized setup to get a clear picture of the possible options for this demonstration experiment. Furthermore, by choosing the right alcohols, we provide a better way to demonstrate that the initial dehydrogenation to the aldehyde is a key step in the entire process.

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■ HAZARDS

All of the used alcohols are highly flammable and rather toxic. Although there is no danger that the explosion continues outside the setup, an appropriate distance between a Bunsen burner and the setup should be maintained when using a flame to preheat the catalyst or the alcohol. Also, an immediate explosion may occur upon inserting the hot catalyst into the flask, and appropriate safety measures should be taken as outlined previously.[1,2,4] Furthermore, the product aldehydes and ketones, small amounts of which will escape from the setup, are toxic and in some cases carcinogenic. Thus, it is highly advised to perform the experiment in a fume hood. Although formaldehyde was detected by its smell, smelling of the reaction mixture should be avoided. Some of the d-block metals are not suitable to use in an oxygen-rich atmosphere at high temperatures. In particular, the use of Cd, Hg, and Os is especially discouraged due to the toxicity of the elements and/or their volatile oxides.

■ EXPERIMENTAL SECTION

Figure 1 schematically shows the apparatus used in our experiments. For reasons of clarity, it does not show the lab jack that supports the hot plate nor the standing clamp holding the Erlenmeyer flask. These additions significantly improve the safety of the setup. The different metal catalysts consisted of spirals of about 1.5 mm diameter made from 10−20 cm long wires with a diameter of 50−200 μm. In the case of Cu, also a mesh (from wire with a similar diameter) was used. Using the mesh is visually attractive as it clearly shows temperature gradients moving around over the catalyst surface.

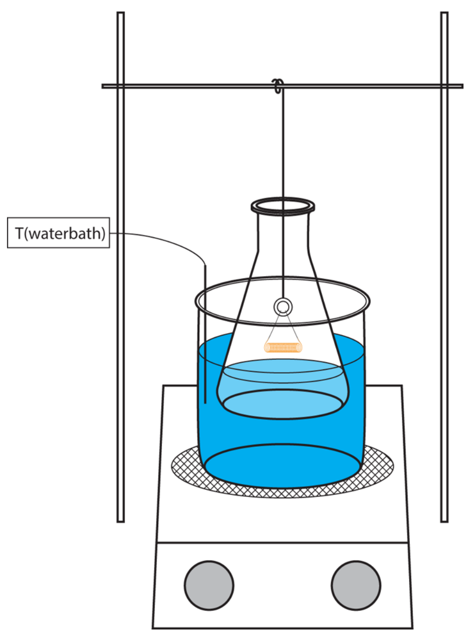

Figure 1. Schematic view of the used setup.

The catalysts are attached to a ceramic ring to isolate them from the steel wire that is used as the handle. This handle was attached to a horizontal bar that is held by two stands from the side. In this way, it is possible to keep the time between preheating the catalyst and starting the experiment as short as possible. It was found to be beneficial for the reactivity when the catalyst was fixed in place such that it could not swing around (especially in the case of an explosion). Possibly, this movement causes a faster heat exchange with the surroundings and thus a lower catalyst temperature.

As described by De Gruijter, the methanol was heated to 50 °C.[3] A water bath with thermostat was used in our experiments to obtain a stable system. However, in a demonstration, the exact temperature is probably less important and one could preheat the methanol using a hot plate or a Bunsen burner to get a better view of the experiment. For a fair comparison between the different alcohols, all were heated to approximately 10 °C below their boiling point, leading to a vapor pressure of around 0.5 bar. The exact temperatures are listed in Table 1. For the experiments with 1-butanol, the water bath was saturated with NaCl to prevent it from boiling.

Table 1. Temperature of the Water Bath Used for the Different Alcohols

alcohol	temperature (°C)
methanol	50
ethanol	50
1-propanol	75
2-propanol	60
1-butanol	95
2-butanol	80
tert-butyl alcohol	70

In some of the descriptions of this experiment, a divider is placed in the Erlenmeyer flask.[1,3] This divider stabilizes the airflow through the glassware and thereby increases the probability of regular explosions of the gas mixture. However, we argue that this explosion is only a "gimmick" of the experiment as it is most probably caused by ignition of the gas mixture due to the temperature of the wire. Indeed, an explosion also typically occurs when putting a very hot catalyst in the Erlenmeyer flask. Thus, the explosion is not really involved in demonstrating the heterogeneous catalysis, which is the goal of this demonstration. In our experiments, no divider was used as we think that once the catalyst is active, it should always be possible to adjust the setup such that explosions will occur. Nevertheless, it should be noted that with our setup, regular explosions were only observed when methanol was used as a reactant. Other reactive alcohols led to a consistently high catalyst temperature as judged from their color, but no explosions were observed within the time frame of the experiment.

■ RESULTS AND DISCUSSION

To get a better overview of the catalytic reactivity of d-block metals toward methanol oxidation, all metals available in our laboratory were considered. Some of those were not tested due to practical issues as toxicity or low melting points. The results on the different metals as a catalyst for methanol oxidation are illustrated in Figure 2. The reactivity was monitored by the color of the glowing metal, which gives a rough indication of the temperature. A metal is considered active once no significant decrease in (average) temperature during the course of the experiment is observed. Each catalyst was tested for at least several minutes to capture multiple temperature oscillations. In the shown transition metal section of the periodic table in Figure 2, it can be seen that the active metals are mainly found in groups 9−11. Iron from group 8 also works. No activity was observed for gold, even when the gold

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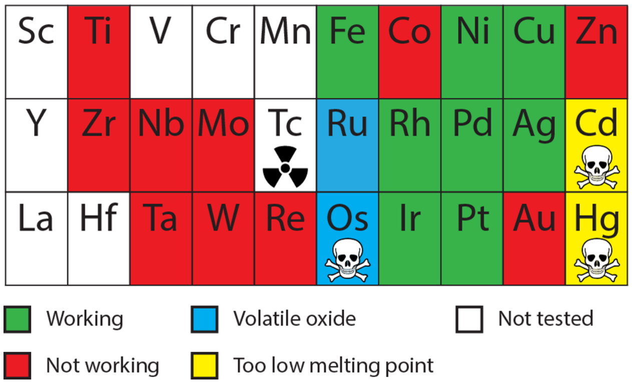

Figure 2. Reactivity of d-block metals toward the oxidation of simple alcohols in the "exploding" flask demonstration. Materials that were considered too hazardous (as indicated by the symbols) were not tested.

wire was preheated to its melting point. However, as the melting point of Ag is lower than that of Au, it can be concluded that gold shows no reactivity. The only other inert metal in groups 9−11 was Co.

These results nicely illustrate general trends in heterogeneous catalysis as often shown through volcano plots, also illustrating the Sabatier principle.[6,7] Transition metals positioned too far to the left in the periodic table bind intermediates and products too strongly to the catalytic surface and are self-poisoning. When positioned too far to the right, the reactants do not dissociate on the catalyst surface. Hence, catalytic activity peaks somewhere between, depending on the details of the reaction.

All of the different metals were tested for their reactivity toward the C_1−C_4 alcohols listed in Table 1. The similarities for the different simple alcohols show an unselectivity as may be expected for heterogeneous catalysts. For all the alcohols except *tert*-butyl alcohol, the reactivity was the same as that for methanol (Figure 1). However, regular explosions only occurred for methanol. No significant systematic changes, such as lower catalyst temperature, could be observed when heavier alcohols were used. Therefore, we have no reason to assume that there is no reactivity toward more complicated or even larger alcohols, such as glycerol, pentanol, etc. However, to maintain a similar vapor pressure, one would need to heat the alcohol beyond the boiling temperature of water. An oil bath would make this possible but also complicates this experiment as a demonstration.

None of the catalysts showed any reactivity toward *tert*-butyl alcohol. This indicates that the alcohol decomposition described in reaction 3 is indeed a crucial step in the overall process. As it is impossible to form a tertiary ketone, this reaction cannot occur for *tert*-butyl alcohol.

In general, it was observed that a higher thermal mass (larger diameter) of the wire has a negative effect on the reactivity. Obviously, this is a nice illustration of the tendency to use nanoparticle catalysts instead of the bulk material. With our approach, it was not possible to draw any quantitative conclusions about the performance of the different catalysts. However, this might be an interesting approach for a classroom experiment. In this case, one should take care to make the catalysts more comparable, for example, in terms of geometrical surface area, area to volume ratio, or thermal mass. If a thermocouple is connected to the catalyst, the performance can be described in terms of temperature or oscillation frequency. In the case of methanol, the time between the explosions might also provide a rather good estimate.

■ CONCLUSION

Using a standardized setup, we provide an extension of the "exploding" flask demonstration by testing the catalytic activity for various combinations of catalysts and reactant alcohols. The reactivity of different d-block metals perfectly illustrates the "sweet spot" in the periodic table where most of the industrially relevant catalysts are found. The reactivity of the different metals was the same toward all tested alcohols except *tert*-butyl alcohol. The fact that no reactivity was observed toward the oxidation of *tert*-butyl alcohol indicates that the decomposition of the alcohol to an aldehyde or ketone is indeed a crucial step in the reaction mechanism. Apart from the extension of the demonstration experiment, this information could also be useful for classroom experiments where students could work on a quantitative comparison between different catalysts, alcohols, and experimental setups.

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Notes

The authors declare no competing financial interest.

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