Misconceptions in the Exploding Flask Demonstration Resolved through Students' Critical Thinking

Spierenburg, R.; Jacobse, L.; Bruin, I. de; Bos, D.J. van den; Vis, D.M.; Juurlink, L.B.F.

Article

Misconceptions in the Exploding Flask Demonstration Resolved through Students' Critical Thinking

Rick Spierenburg, Leon Jacobse,[*] Iris de Bruin, Daan J. van den Bos, Dominique M. Vis, and Ludo B. F. Juurlink

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

ABSTRACT: As it connects to a large set of important fundamental ideas in chemistry and analytical techniques discussed in high school chemistry curricula, we review the exploding flask demonstration. In this demonstration, methanol vapor is catalytically oxidized by a Pt wire catalyst in an open container. The exothermicity of reactions occurring at the catalytic surface heats the metal to the extent that it glows. When restricting reactant and product gas flow, conditions may favor repetitive occurrence of a small explosion. We show how mass spectrometry and infrared spectroscopy allow for unravelling the chemical background of this demonstration and discuss various ideas on how to use it in a classroom setting to engage students' critical thinking about chemical research. Along the way, we show that two commonly published ideas about the chemical background of this demonstration are incorrect, and we suggest simple tests that may be performed in a high school setting either as an addition to the demonstration or as a student research project.
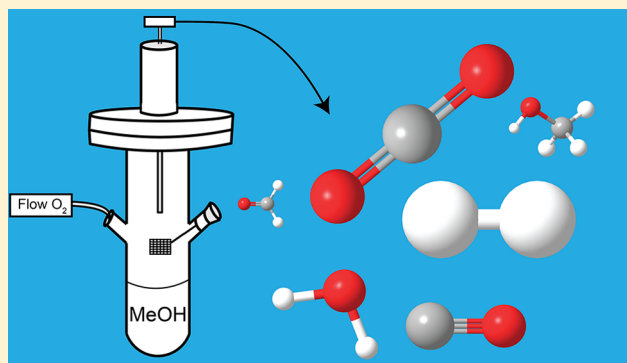
KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Physical Chemistry, Misconceptions/Discrepant Events, Hands-On Learning/Manipulatives, Alcohols, Catalysis, Metals, Qualitative Analysis*

INTRODUCTION

There are, at most, a few good demonstrations that illustrate principles of heterogeneous catalysis. The "exploding flask" demonstration is probably the best known example.[1−4] A preheated catalyst wire is suspended over a thin layer of liquid methanol and catalytically oxidizes its vapor. The oxidation reaction is exothermic enough to make the catalyst wire glowing hot. Using an Erlenmeyer flask instead of a beaker restricts replenishment of consumed O_2 from the air. Repetitive explosions may occur. The intensity of the explosion can be increased using a divider in the neck of the Erlenmeyer flask.[1,3] When a beaker is used, the catalyst may remain visibly hot, but no explosions are observed.[2] YouTube provides various video examples of this demonstration, generally based on Pt as the catalyst material.[5−8] Other metals may be used though. De Gruijter used copper.[3] Battino et al. showed that Pd, Ni, Ni/Cu, and Ag also work,[1] whereas Weimer claimed that Cu, Al, Fe, and Ni show no reactivity at all,[4] a systematic comparison for a wide range of metal catalysts and various $C_1–C_4$ alcohols showed that Fe, Rh, Ir, Ni, Pd, Pt, Cu, and Ag all catalyze the oxidation of simple primary and secondary alcohols in this demonstration. Only for tert-butanol, no reactivity was observed.[9]

The demonstration is visually attractive and has a number of easily tested variables, that students may propose when asked for minor alterations that could help in learning to investigate general aspects of the chemical reaction. Catalyst material, the fuel, gas flow restriction, distance between catalyst and the liquid level, and the temperature of the liquid all affect the demonstration's observables. All of these directly or indirectly affect the kinetics of the reaction either through changes in the (relative) concentrations of reactants or the catalytic activity of the material toward combustion of the specific fuel. There is, however, another major benefit to implementing this demonstration in a high school curriculum. When continuing the classroom discussion following the demonstration, questions that relate to and connect many aspects of the curriculum will arise. How do gas flow conditions, thus stoichiometry, result in absence or presence of repeated explosions? What is exploding? Is it the methanol vapor? What is that pungent smell? Formaldehyde? What is causing the glow of the solid catalyst wire, whereas the chemistry, as written down in a chemical equation, contains only gas phase reactants and products? While a survey of the literature suggests that experimental variables have been explored rather well for this demonstration, the provided explanations, among others in this *Journal*, are highly doubtful. A guided classroom discussion will bring this to light. We discuss two obvious questions within the framework of such a classroom discussion, assuming a knowledge level characteristic for students nearing graduation.
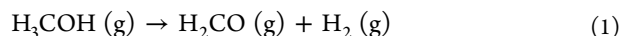
■ WHAT ARE THE (ELEMENTARY) CHEMICAL REACTIONS UNDERLYING THIS DEMONSTRATION?

Multiple authors claim that the key reaction in this demonstration, as performed with methanol, is its decomposition to formaldehyde:[1,2]

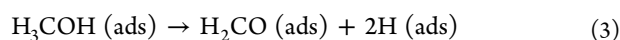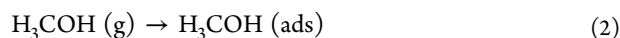$$H_3COH\ (g) \rightarrow H_2CO\ (g) + H_2\ (g) \tag{1}$$

This claim arises from the pungent smell that may be observed when being (too) close to the reaction vessel. However, one can point out that formaldehyde can be smelled at very low concentrations.[10] In combination with the observed hot catalyst wire, it is actually impossible that it is the major product as the decomposition of methanol to formaldehyde in reaction 1 is endothermic. Students can check the reaction enthalpy calculation within seconds as CH_3OH and CH_2O are generally very close in standard thermodynamic tables and the only other product is an element. Formaldehyde may therefore be no more than a (minor) side product of the reaction. This poses the question what (elementary) chemical reactions occur at the catalyst surface that explain both the formation of CH_2O and the obvious heating of the Pt wire.

Starting with the known product H_2CO, the reactions that must occur are schematically illustrated in Figure 1.
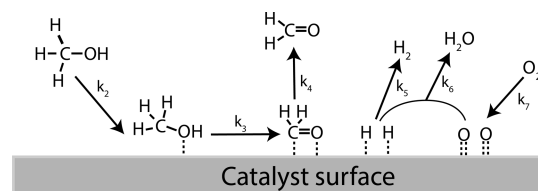
Figure 1. Catalytic reaction of methanol on a Pt surface. Reaction rate constants are labeled in accordance with reactions appearing in the text.

Upon impinging onto the Pt surface from the gas phase, CH_3OH dehydrogenates. If it only loses 2 H atoms that individually bind to the surface, the remaining adsorbed H_2CO moiety can desorb intact, explaining the pungent smell. The adsorbed H atoms form H_2 (g) by recombinative desorption. By neglecting the reverse reactions, the overall reaction may thus be written as a simple summation of

$$H_3COH\ (g) \rightarrow H_3COH\ (ads) \tag{2}$$

$$H_3COH\ (ads) \rightarrow H_2CO\ (ads) + 2H\ (ads) \tag{3}$$

$$H_2CO\ (ads) \rightarrow H_2CO\ (g) \tag{4}$$

$$2H\ (ads) \rightarrow H_2\ (g) \tag{5}$$

These surface reactions, especially the adsorption on and desorption of hydrogen at Pt, most commonly on the Pt(111) and vicinal surfaces, are extremely well studied in the catalytic and surface science communities, among others by ourselves.[11−14] This reaction has served as the model system to the surface science and reaction dynamics communities in testing basic theoretical assumptions, for example, the Born−Oppenheimer approximation, for breaking a single bond.[15] Adsorption to and the subsequent decomposition of methanol on Pt (see, e.g., refs 16−18) as well as H_2CO (see, e.g., ref 19) have been studied. Reactions 2−4 explain the appearance of the pungent smell in the demonstration, but they do not explain

that the Pt wire remains hot throughout the demonstration as the overall reaction 1 is endothermic.

An exothermic surface reaction is required for the catalyst to remain hot or even increase in temperature in between explosions when oscillatory behavior is observed. When asked, students are likely to recognize that the H_2 (g) from reaction 1 can be combusted, yielding heat. As it is obviously the wire that becomes very hot, the combustion must, however, occur at the surface of the metal. This catalyzed chemical reaction is thus the oxidation of surface-bound atomic hydrogen produced from reaction 3:

$$2H\ (ads) + O\ (ads) \rightarrow H_2O\ (g) \tag{6}$$
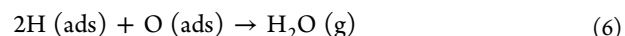
Catalytic oxidation of hydrogen by Pt is also considered a model system and has been studied extensively using the surface science approach (see, e.g., refs 20−23). The required surface-bound atomic oxygen arises from dissociative adsorption of O_2 (g) on the Pt catalyst, which in itself is also well-studied (see, e.g., refs 24−28):

$$O_2\ (g) \rightarrow 2O\ (ads) \tag{7}$$

Having introduced the left part of the surface reactions shown in Figure 1, students may be expected to come up with reactions 6 and 7 when asked. Now, students may be asked to calculate using their thermodynamic table whether the additional oxidation by O_2, or in other words the partial oxidation of methanol to formaldehyde in air, may explain the continuous glowing of the catalyst wire.

At this point, one may diverge into different directions to discuss various related chemical principles. For example, one could ask students for the expected effects when changing the relative concentrations of O_2 (g) and CH_3OH (g). Experimentally, this is done, for example, by restricting the air flow, additional heating of the liquid, or changing the position of the catalyst wire relative to the air-conducting orifices and the liquid level. As the concentrations affect the rates of dehydrogenation versus partial oxidation of methanol, this opens up the opportunity to introduce the difference between two of the three most important concepts in heterogeneous catalysis: reactivity toward a reactant and selectivity toward a desired product. In an oxygen-deficient environment, H_2 will build up. In an oxygen-rich environment, the partial oxidation is likely to dominate, and H_2O will be formed at the expense of H_2. One could also take the discussion in the direction of the different catalytically active materials that can be used in this demonstration. The required dissociative adsorption of O_2 varies with the type of metal. Copper is known to oxidize fairly easily and extensively (think of the Statue of Liberty), whereas Ag and Pt do not and are therefore used as jewelry.

Whatever the course of the discussion, it is noteworthy that selective dehydrogenation of methanol to formaldehyde turns out to be difficult. In industry, it is generally performed using a Ag or Fe−Mo oxide catalyst (see ref 29 and references therein). A large fraction of methanol is unfortunately lost to byproducts. What byproducts would students expect? It is likely that, in parallel to desorbing, formaldehyde reacts further on the Pt catalyst surface:

$$H_2CO\ (ads) \rightarrow CO\ (ads) + 2H\ (ads) \tag{8}$$
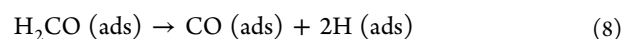
The surface-bound CO may either desorb intact or, depending on the availability of surface-bound O atoms, also be oxidized to CO_2, thus giving complete oxidation of methanol to CO_2:

$$CO \ (ads) \rightarrow CO \ (g) \tag{9}$$

$$CO \ (ads) + O \ (ads) \rightarrow CO_2 \ (g) \tag{10}$$
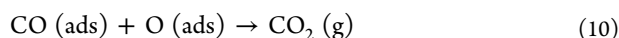
These processes are illustrated in Figure 2.
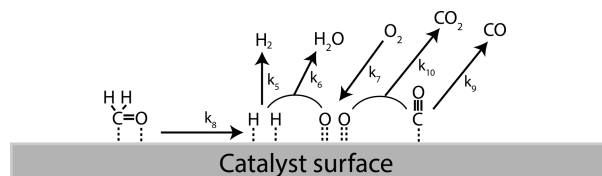
Figure 2. Schematic illustration of catalytic dehydrogenation of H_2CO on a Pt surface in combination with potential oxidation of surface-bound products. Reaction rate constants are labeled in accordance with reactions appearing in the text.

The oxidation of CO in reaction 10 provides additional heat to the catalyst surface and is, in part due to its extremely high turnover frequency, probably the most studied reaction in the surface science community (see, e.g., ref 30 and references therein). Students could again use their thermodynamic table to compare the heats of reaction for the various partial and complete combustions.

A recent density functional theory study of methanol oxidation on Pt outlines the energy profile of the reaction up to the formation of CO.[16] Combined with other studies,[31,32] we estimate the energy profile for the complete oxidation on the most abundant surface plane of Pt, that is, Pt(111), in Figure 3.
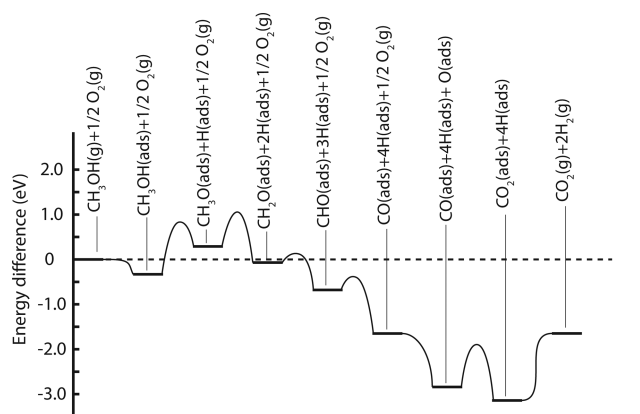

Figure 3. Energy profile for complete catalytic combustion of CH_3OH on Pt(111) based on refs 16, 31, and 32.

We provide it here, as in a classroom setting, it may be used to illustrate the continuing downward energetic path for this reaction beyond the initial dehydrogenation of CH_3OH. Hence, the path should favor formation of CO or CO_2 via reactions 8, 9, and 10 at the expense of H_2CO desorption, that is, reaction 3. As CO and CO_2 have no smell, they go by undetected to a demonstrator relying only on olfactory detection of gaseous products. This allows a teacher to pose the question how one could experimentally investigate which products are made and how much of each of them. If previously discussed, students may give answers, for example, mass spectrometry and infrared spectroscopy for identification or quantitative analysis of gaseous products. In the Experimental Section, we provide data that may be used and also serve to show that the use of a

single experimental technique may often not allow for answering scientific questions in full.

WHAT IS THE CAUSE OF THE EXPLOSIONS?

Besides the incomplete consideration of surface chemical reactions, the literature is only speculative on the origin of the gas phase explosions that may be induced in this demonstration. Without providing evidence, it is generally ascribed to methanol vapor.[5,6,8] However, considering the reaction mechanism provided above, H_2 is likely present in the gas phase. The relative rates of H_2 production from reaction 5 and the consumption of atomically bound H in reaction 6 will vary with surface temperature. Reactions 3 and 8 provide the atomic, surface-bound H atoms. Hence, the H_2 (g) concentration will vary with surface temperature and may just as well lead to a situation where the gas phase explosion limit of an H_2/O_2 mixture is reached:

$$2H_2 \ (g) + O_2 \ (g) \rightarrow 2H_2O \ (g) \tag{11}$$
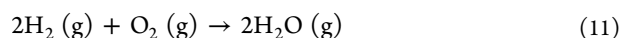
The mechanism of this reaction in the gas phase is complex, involves multiple radical species (see, e.g., ref 33), and may be initiated by H or O atoms emitted from the Pt catalyst at high temperature. Pt is used in scientific laboratories as a source of gas phase O atoms from dissociative adsorption of O_2 followed by emission of O (g). The same mechanism probably produces H atoms, although generally one would use hot W as the source of H atoms as tungsten is considerably cheaper and has a higher melting point. Notably, the concentration range where methanol forms an explosive mixture (between the lower and higher explosion limit), is much narrower (6.7−36.0 vol %) than for hydrogen (4.0−75.0 vol %).[34] The expected vapor pressure of methanol inside the flask with a liquid temperature of 50 °C is 0.55 bar. Hence, the gas mixture is too rich in methanol to be explosive, which supports the suggestion that hydrogen is responsible for the explosion. Although this may exceed the appropriate level for a discussion in a high school situation, the essential idea that the composition of the gas mixture inside the vessel depends on the details of gas flow, catalyst temperature, etc. are surely within reach. One could ask students to formulate a hypothesis. If standard analytical techniques have been discussed previously, students may also be asked how they would investigate the chemical composition of the gas mixture in the vessel, for example, prior to, during or after the explosions, and what results would prove their hypothesis.

In the following, we describe how we have studied this demonstration with second-year undergraduate students at Leiden University in The Netherlands using parts of regular scientific (ultrahigh vacuum, UHV) equipment (see, e.g., ref 35) for mass spectrometry (MS) and infrared (IR) spectroscopy. Such equipment is generally not available at high schools. For this reason, we present our data such that they may be used as part of a classroom discussion or in written examples or exercises. Also, we have experimented with much simpler equipment and indicator reagents that are available at high schools and easily provide qualitative proof and allow students to arrive at the same conclusions regarding the chemical background of the exploding flask demonstration.

EXPERIMENTAL SECTION

Figure 4 schematically represents our system used to probe gaseous products during Pt-catalyzed methanol oxidation by
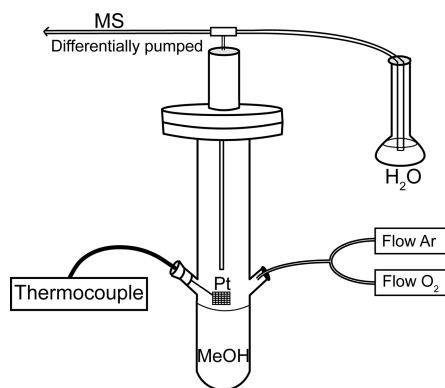
Figure 4. Setup used to sample the gas mixture for MS. The temperature of the Pt gauze catalyst is read out using a thermocouple. The overpressure is released via a bubbler, while the composition of the product stream is determined by a differentially pumped mass spectrometer.

MS. It consists of a glass reaction tube with two necks positioned on opposite sides and a glass-to-metal connection at the top. Through the top flange, a stainless steel tube protrudes into the vessel. It samples the gas mixture just above the catalyst. The sampled gas stream is split. One part is led toward a differentially pumped quadrupole mass spectrometer (QMS, Pfeiffer QME200). The other part enters a bubbler, preventing the system from pressurizing and capturing potentially toxic, water-soluble vapors. The liquid methanol is kept at 50 °C using a water bath and thermostat (Heidolph MR Hei-Standard, not shown in Figure 4). Just above the liquid surface, a polycrystalline Pt gauze (0.04 mm diameter wire) is positioned through one of the two necks. It is heated in a blue butane flame prior to insertion. A type-K thermocouple, spot-welded to the catalyst, measures the temperature. It is read out using a PID controller (Eurotherm 2416). To control the O_2 concentration, a mixture of O_2 and Ar is provided through the other neck into the reaction vessel using flow controllers (Brooks F-201C and Brooks 5850TR). The Ar carrier gas replaces the unreactive N_2 from air and serves as an internal standard in case the QMS shows intensity drift. It also reduces the chance of formation of NO_x during explosions. The volume of the system is approximately 800 mL.

An FTIR spectrometer (Bruker VERTEX 70) is used for IR identification of gaseous products. A rotary vane pump evacuated an IR cell with NaCl windows placed inside the FTIR spectrometer. The vacuum was used to draw the gas mixture from the standard demonstration equipment (as depicted in ref 1), where we replaced the Erlenmeyer flask with a Büchner flask. A short tube with a valve connected the IR cell and the Büchner flask, ensuring little loss and a short transfer time. Gas was drawn into the IR cell when the catalyst was glowing hot or immediately after explosions when the Pt catalyst was rapidly cooling. IR experiments were performed with methanol kept at a constant temperature of 50 °C and a preheated Pt catalyst wire.

The presence of CO_2 as a product may be verified qualitatively with limewater. A transparent, saturated solution of $Ca(OH)_2$ becomes turbid in the presence of CO_2. Figure 5 schematically illustrates how we adapted the demonstration equipment to this purpose. We used a three-necked flask, positioned with a stand, and containing a layer of methanol kept at 50 °C by a water bath. One neck of the flask was
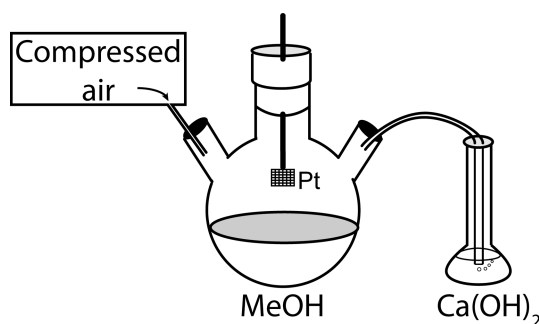
Figure 5. Schematic drawing of the setup used for indicating CO_2. The compressed air drives the reaction mixture through the limewater.

connected to a bubbler filled with limewater. Through another neck, compressed dry air was introduced. A preheated Pt catalyst was hung from a septum, which closed the system.

Similar to limewater indicating CO_2, Tollens' reagent can be used to show the presence of aldehydes.[36,37] This reagent was prepared by adding excess 2 M KOH (BOOM) solution to 0.05 M $AgNO_3$ (ACROS ORGANICS) solution forming insoluble Ag_2O, and then adding excess 2 M NH_4OH (Riedel-de Haën) forming soluble $[Ag(NH_3)_2]NO_3$. This complex is colorless in solution. Reduction to metallic silver by aldehydes yields a dark, metallic coloring of the solution. We used the equipment shown in Figure 5 with $Ca(OH)_2$ being replaced by Tollens' reagent.

■ HAZARDS

The risks related to the exploding flask demonstration in general have been described extensively in the literature.[1,2,4,9] In short, the used chemicals and the reaction products pose risks due to their toxicity and flammability. The demonstration should be performed in a well-ventilated area, preferably a fumehood. Extra care should be taken while heating the catalyst or alcohol with a flame. Some additional remarks are necessary for the specific extensions of the experiment described here. When using a closed system, care should be taken not to overpressurize the system and to prevent the occurrence of explosions of the gas mixture. It is recommended to put appropriate shielding in place, especially when tuning the gas flow. Tollens' reagent should not be stored longer than strictly necessary as the highly explosive silver nitride is formed during its degradation.[36]

■ RESULTS AND DISCUSSION

Results Using Scientific Laboratory Equipment

Figure 6 shows background-corrected mass spectra obtained without (blue) and with (red) the hot Pt catalyst present in the reaction vessel under otherwise identical conditions while no explosions occurred. The two spectra are normalized to the Ar partial pressure using the integral of the peak at $m/z = 40$ (Ar^+). The appropriateness of this correction is demonstrated by the resulting perfect overlap of the peak appearing at $m/z = 20$ (Ar^{2+}). Figure 6 shows the tenth spectrum after insertion of the Pt catalyst in comparison to the spectrum without the catalyst from a continuous series of spectra, each requiring 60 s to collect. After this amount of time, initial changes in the gas composition resulting from letting in air when inserting the catalyst have mostly disappeared, the spectrum is stable and may be interpreted quantitatively. The two spectra differ clearly with respect to $m/z = 2$, 28−32, and 44. Minor differences are
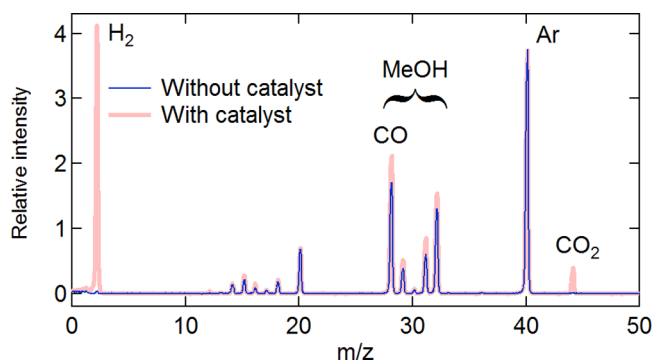
Figure 6. Mass spectra of the gas composition in the reaction vessel for methanol heated to 50 °C and a 45 vol % O_2 and 55 vol % Ar stream at 83 mL/min flow rate without (blue) and with a Pt catalyst at 660−680 K (light red) present.

also observed for m/z = 18, 17, 16, 15, and 12. The peaks in the regime m/z = 28−32 require a detailed analysis as they may result from multiple species.

Figure 6, without the chemical labels, may be used to test students' ability to interpret mass spectra and discuss the implications toward the chemical background of the exploding flask demonstration. For example, the spectrum without the catalyst present may be used to assign chemicals introduced into the vessel; m/z = 40 for Ar^+, m/z= 32 for CH_3OH^+, and the same for O_2^+. Subsequently, the changes in the spectrum can be assigned. The large peak at m/z = 2 can only be assigned to H_2^+ and the peak at m/z = 44 is assigned to CO_2^+. In relation to the chemical mechanism underlying the demonstration, the appearance of peaks at m/z = 2 and 44 when the Pt catalyst is inserted proves that H_2 and CO_2 are formed catalytically by Pt in significant quantities. The minor increase for m/z = 18 may be asked to be ascribed to prove the formation of H_2O^+. In case MS fragmentation has been discussed (as, e.g., in Dutch VWO and the International Baccalaureate Chemistry syllabi), the increase in m/e = 12 (C^+), 16 (O^+) may be asked to be related to fragmentation of CO_2^+ and 17 (OH^+) and 16 (O^+) to H_2O^+. Other minor changes in the spectrum that may be related to catalytic formation of CO and H_2CO require more scrutiny of the spectrum as described below.

Figure 7 shows three mass spectra over the range of m/z = 27 to 33. Let us consider the possible contributors to these peaks in the red spectrum, that is, when there is no chemical
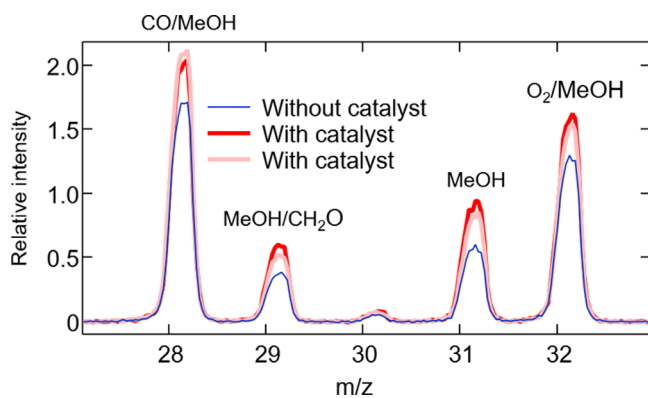
Figure 7. Mass spectra of methanol at 50 °C with the Pt catalyst in for 300 s (dark red), 600 s (light red), and without catalyst (blue).
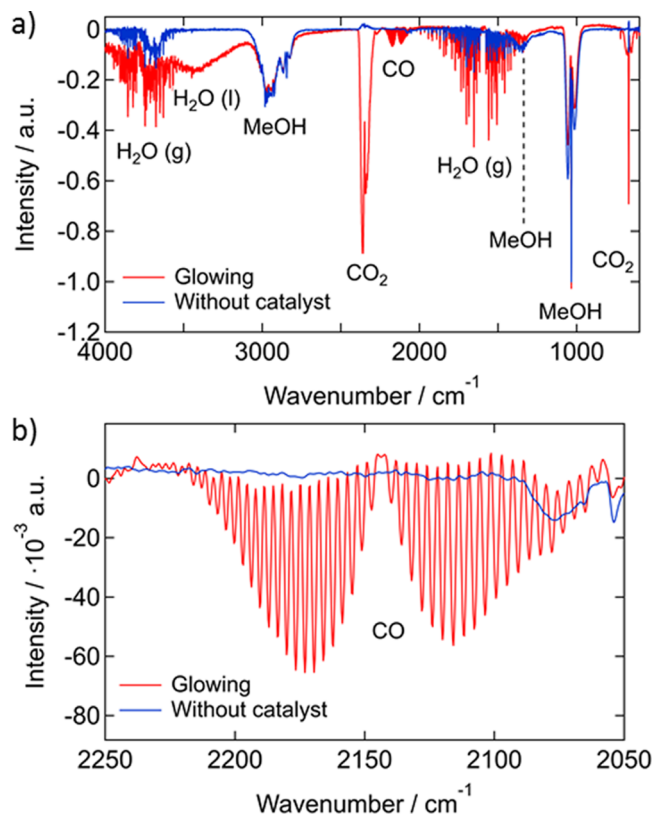
reaction for a lack of the Pt catalyst. First, CH_3OH is present abundantly due to heating the liquid to a temperature only 15 K below its boiling point. The parent ion of methanol, H_3COH^+, (m/z = 32) is rather unstable and fragments in the QMS ionizer to H_3CO^+ (m/z = 31), H_2CO^+ (m/z = 30), HCO^+ (m/z = 29), and CO^+ (m/z = 28). Hence, each peak in the red spectrum contains a contribution of methanol. The peak at m/z = 32, however, also contains a contribution of O_2^+, which is added as a reactant via the O_2/Ar stream.

When the Pt catalyst is added to the system, consumption of CH_3OH would lead to a drop to the intensity of *all* peaks in this part of the spectrum. However, production of H_2CO (g) from consecutive reactions 3 and 4 would (approximately quantitatively) counterbalance the drop for m/z = 30, 29, and 28 from creation of H_2CO^+, HCO^+, and CO^+. Catalytic production of CO via reactions 8 and 9 would also compensate at m/z = 28 (CO^+). The same peak however also reflects CO_2 from fragmented CO_2^+. Hence, catalytic dehydrogenation and oxidation would probably not affect peaks at m/z = 28, 29, and 30 much. However, this would not be the case for m/z = 31, which is unique to CH_3OH. One can easily image a question for students regarding this exception.

As can be judged from the spectrum in Figure 7, the experiment suffered from another complication that makes it difficult to judge by MS whether CO and H_2CO are produced. All peaks actually increase. This is the result of local heating of the liquid methanol when the hot Pt catalyst (its temperature being on the order or 500−1000 K) is introduced ∼1 cm above the liquid−gas interface. The increased vapor pressure affects all peaks in a nearly identical way. There is only one exception when judging the differences after 300 (dark red) and 600 s (light red). Although for all peaks between m/z = 29 and 32, the methanol contribution has dropped a minor amount (dark being lower than light red), the change is inversed for m/z = 28. It is tempting to consider this proof that CO is being formed from CH_3OH. However, only the very bright student will recall that changes in m/z = 28 may also reflect variations in production of CO_2. Hence, MS only provides clear evidence that the exploding flask demonstration produces CO_2 and H_2 and hints at the production of H_2O.

As vibrational spectroscopy is generally also discussed in high school syllabi, we investigated the product gases using an FTIR. Integrated intensity bands for CH_3OH and H_2CO are rather similar and also CO_2 and CO are easily detected with characteristic frequencies uniquely identifying each species. Figure 8a shows IR absorbance spectra of gas drawn from the Büchner flask before introducing a Pt wire into the system and when the catalyst is present and glowing. Without the catalyst, strong absorbances near 1000, 1600, 3000, and 3700 cm^{-1} appear. The peaks around 1000 and 3000 cm^{-1}, as well as the smaller peak around 1300 cm^{-1}, result from methanol vapor. The bands around 1600 and 3700 cm^{-1} are related to the presence of gas phase water. For comparison, the spectra were normalized to the peak around 1000 cm^{-1}, which led to a good overlap of the other methanol peaks.

After introducing the glowing Pt wire, the gas phase water peaks increase in intensity and several additional peaks are observed. The peaks around 2380 and 800 cm^{-1} can be ascribed to CO_2, confirming our conclusion from the mass spectrometry measurements. In addition, when zooming in at the area around 2140 cm^{-1} (shown in Figure 8b), the characteristic absorbance of CO is found. The P- and R-branches are even rovibrationally resolved. The broad feature

Figure 9. Infrared spectra of the gas mixture resulting from oxidation of methanol with Pt catalyst while the catalyst is glowing (red) and immediately after an explosion.


Figure 8. (a) IR spectra of methanol at 50 °C without (blue) and with (red) a glowing Pt catalyst; (b) enhanced IR spectra of methanol at 50 °C without (blue) and with (red) a glowing Pt catalyst.

around 3500 cm^{-1} results from liquid water, which condensed on the windows of our IR cell, its intensity also varying in each experiment. Hence, the combination of IR and MS studies prove that the exploding flask demonstration produces CO_2, CO, H_2, and H_2O.

If formaldehyde was present in the gas phase at concentrations comparable to CO, its characteristic peaks near 2850, 1750, and 1165 cm^{-1} should be observable. From these, only the latter has no overlap with the other peaks in the spectra. When zooming in at the area around 1165 cm^{-1}, no peak is observed. Even the integrated spectra, which corrected for the absorption cross-sections contain quantitative information on the detected molecules, show no indication of a peak in this area. Thus, the only possible conclusion is that the amount of formaldehyde produced is extremely small.

When allowed to use a reference book, provided with a table of typical absorption frequencies, or with already assigned peaks in these spectra (as in Figure 8), students may be asked to discuss the absorption spectra prior to and after insertion of the catalyst. Their assignment of the peaks and consideration of the changes allows them to arrive at the same conclusion that, beyond olfactory identification of formaldehyde, there is no evidence of it being an important product or intermediate in the chemical background of the exploding flask demonstration.

Finally, Figure 9 shows IR spectra taken when the catalyst was glowing (red) and immediately after an explosion occurred (green). Much like the spectra in Figure 8, the characteristic peaks of products CO and CO_2 appear as well as remaining reactant CH_3OH. As the amount of gas sampled from the reaction vessel varied slightly from experiment to experiment, our spectra should not be interpreted quantitatively here.
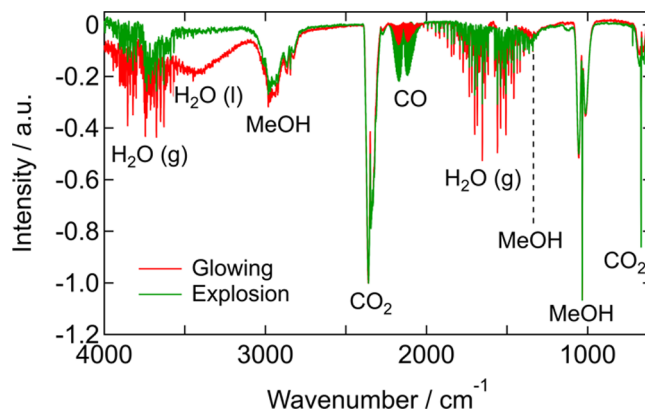
However, relative changes allow the student to get one step further in understanding the demonstration. To do so, we normalized the spectra in Figure 9 to the CO_2 peak at 2380 cm^{-1}. From these data, it can be determined that after the explosion, the CO/CO_2 ratio has increased with a factor 3.5. This suggests either a lack of O_2 required for CO oxidation (presumably because of its consumption in the gas phase explosion) or a changed product selectivity resulting from different temperature-dependencies of k_9 and k_{10} as the temperature of the catalyst drops on the order of several hundreds of degrees after the explosion. On a similar note, one might argue that the relative amount of H_2O (g) decreases, but this difference is much more subtle. As in the case with the glowing catalyst, the explosion does not produce a detectable amount of formaldehyde.

Result Using High School Accessible Equipment

The experiment performed with the apparatus shown in Figure 5 with methanol kept at 50 °C showed turbidity of the limewater solution within minutes. Although qualitative by nature, the experiment reinforces that CO_2 is a major product of the chemical reactions occurring in this demonstration. When repeating the experiment with Tollens' reagent, it also turned cloudy. However, we did not find any sufficient reference to the selectivity of this reagent to formaldehyde, other aldehydes, and other species possibly present in our gas mixture. Thus, we verified whether the same reagent would also react with CO, CO_2, methanol, and the used pressurized air. Unfortunately, Tollens' reagent also reacts with CO. Hence, it cannot be used to discriminate between CO and formaldehyde. However, with a working catalyst the reagent turned cloudy within a few minutes, while this took a few seconds for the CO experiment. This suggests that the concentration of molecules reacting with Tollens' reagent in our reaction mixture is on the order of a few per mille. As formaldehyde becomes irritating at concentrations above 1.0 ppm, it seems highly likely that CO is formed at significant concentrations.

■ CONCLUSION

Experimental results clearly indicate that the surface chemistry underlying the heterogeneous catalysis demonstration is significantly more complex than claimed previously. From all possible paths in the network of parallel reactions of surface-bound intermediates (desorption versus decomposition of CH_2O_{ads}, desorption versus oxidation of H_{ads}, and desorption

versus oxidation of CO_{ads}), two reaction paths seem dominant: recombinative desorption of H_2 produced from sequential dehydrogenation of CH_3OH to CO_{ads} and the complete oxidation of the methanol's carbon atom to CO_2. IR spectroscopy clearly identifies CO as a product. The selectivity toward partial oxidation seems higher following an explosion. This is rather logical as O_2 must be consumed in the explosive gas phase oxidation processes, which compete with dissociative adsorption of O_2 on the catalyst surface. The abundant presence of H_2 in the gas phase and the very low H_2/O_2 explosion limit make it likely that the catalytic dehydrogenation of methanol is the cause of formation of an explosive mixture. The cause is not the presence of methanol and oxygen in the gas phase, which do not change much throughout the cycle as evidenced by only minor changes in mass spectra. Finally, formation of CH_2O is confirmed by its typical smell when opening the apparatus, but its absence in IR spectra and very low olfactory detection limit suggest that it is a minor side product.

We conclude with the notion that this demonstration has beautiful complexity and wide applicability veiled by an apparent simplicity. It requires very few materials, available at nearly every high school, and provides clear, straightforward observations. Addition of the limewater bubbler can be used to show that CO_2 is formed in addition to the CH_2O which can be smelled. This can be used as an illustrative introduction of topics, for example, parallel reactions in kinetics and selectivity, in addition to it visualizing important aspects of heterogeneous catalysis. Other topics, for example, stoichiometry and gas phase reactions (explosions), mass and heat transfer, diffusion, and convection are also directly related and can be incorporated in discussions with students. Finally, rather simple variations of the experiment allow for extensive student research, either as an individual project or for entire classes. For example, one could research the effect on the intensity or frequency of the explosion by changing, for example, temperature of the liquid fuel, the position of the catalyst relative to the liquid surface and the inlet of the O_2, and the shape and size of a divider.[1,3] In our parallel tested demonstration in this issue, we show that a large number of different fuels can be used and which transition metals catalyze their combustion using the same equipment (see ref 9). Readers interested in kinetic studies of CH_3OH reactions over well-defined Pt surfaces are referred to a recent study performed under somewhat lower pressure conditions.[38]

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: l.jacobse@chem.leidenuniv.nl.

ORCID ⊙

Leon Jacobse: 0000-0002-2825-0963

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Battino, R.; Letcher, T. M.; Rivett, D. E. A. The Repeating "Exploding" Flask: A Demonstration of Heterogeneous Catalysis. *J. Chem. Educ.* **1993**, *70* (12), 1029.

(2) Coffing, D. L.; Wile, J. L. The Platinum-Catalyzed Decomposition of Methanol: A Deceptive Demonstration. *J. Chem. Educ.* **1993**, *70* (7), 585−586.

(3) de Gruijter, J. *Show de Chemie*; Kramers-Pals, H., van Schravendijk, J., Bouma, H., de Gen, M. M. J., Eds.; Nederlandse

Vereniging voor het Onderwijs in de Natuurwetenschappen (NVON): Utrecht, 2008; pp 20−21.

(4) Weimer, J. J. An Oscillating Reaction as a Demonstration of Principles Applied in Chemistry and Chemical Engineering. *J. Chem. Educ.* **1994**, *71* (4), 325.

(5) Periodic Videos. *Platinum (version 2) - Periodic Table of Videos*; YouTube, 2010. https://www.youtube.com/watch?v=bBBy4-0uUC4 (accessed June 2017).

(6) Royal Society of Chemistry. *Fire and Flame 32 - Platinum with Methanol*; YouTube, 2013. https://www.youtube.com/watch?v=A2VpA_301rg (accessed June 2017).

(7) Harvard Natural Sciences Lecture Demonstrations. *Platinum Catalysis*; YouTube, 2010. https://www.youtube.com/watch?v=FSdBB1vBDKY (accessed June 2017).

(8) High, H. *Catalytic Decomposition of Methanol*; YouTube, 2012. https://www.youtube.com/watch?v=rsIhjinuBYA (accessed June 2017).

(9) Jacobse, L.; Vink, S.; Wijngaarden, S.; Juurlink, L. B. F. Heterogeneous Catalytic Oxidation of Simple Alcohols by Transition Metals. *J. Chem. Educ.* **2017**, DOI: 10.1021/acs.jchemed.6b00909.

(10) Leonardos, G.; Kendall, D.; Barnard, N. Odor Threshold Determinations of 53 Odorant Chemicals. *J. Air Pollut. Control Assoc.* **1969**, *19* (2), 91−95.

(11) Groot, I. M. N.; Kleyn, A. W.; Juurlink, L. B. F. Separating Catalytic Activity at Edges and Terraces on Platinum: Hydrogen Dissociation. *J. Phys. Chem. C* **2013**, *117* (18), 9266−9274.

(12) Groot, I. M. N.; Kleyn, A. W.; Juurlink, L. B. F. The Energy Dependence of the Ratio of Step and Terrace Reactivity for H_2 Dissociation on Stepped Platinum. *Angew. Chem., Int. Ed.* **2011**, *50* (22), 5174−5177.

(13) Poelsema, B.; Lenz, K.; Comsa, G. The Dissociative Adsorption of Hydrogen on Pt(111): Actuation and Acceleration by Atomic Defects. *J. Chem. Phys.* **2011**, *134* (7), 74703.

(14) Christmann, K.; Ertl, G. Interaction of Hydrogen with Pt(111): The Role of Atomic Steps. *Surf. Sci.* **1976**, *60* (2), 365−384.

(15) Nieto, P.; Pijper, E.; Barredo, D.; Laurent, G.; Olsen, R. A.; Baerends, E.-J.; Kroes, G.-J.; Farías, D. Reactive and Nonreactive Scattering of H_2 from a Metal Surface is Electronically Adiabatic. *Science* **2006**, *312* (5770), 86−89.

(16) Greeley, J.; Mavrikakis, M. Competitive Paths for Methanol Decomposition on Pt(111). *J. Am. Chem. Soc.* **2004**, *126* (12), 3910−3919.

(17) Duke, A. S.; Galhenage, R. P.; Tenney, S. A.; Ammal, S. C.; Heyden, A.; Sutter, P.; Chen, D. A. *In Situ* Ambient Pressure X-ray Photoelectron Spectroscopy Studies of Methanol Oxidation on Pt(111) and Pt−Re Alloys. *J. Phys. Chem. C* **2015**, *119* (40), 23082−23093.

(18) Sexton, B. A. Methanol Decomposition on Platinum (111). *Surf. Sci.* **1981**, *102* (1), 271−281.

(19) Henderson, M. A.; Mitchell, G. E.; White, J. M. The Decomposition of Formaldehyde on Pt(111): A TPD and hreels Study. *Surf. Sci.* **1987**, *188* (1), 206−218.

(20) Gland, J. L.; Fisher, G. B.; Kollin, E. B. The Hydrogen-Oxygen Reaction over the Pt(111) Surface: Transient Titration of Adsorbed Oxygen with Hydrogen. *J. Catal.* **1982**, *77* (1), 263−278.

(21) Michaelides, A.; Hu, P. Catalytic Water Formation on Platinum: A First-Principles Study. *J. Am. Chem. Soc.* **2001**, *123* (18), 4235−4242.

(22) van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. Co-Adsorption of O and H_2O on Nanostructured Platinum Surfaces: Does OH Form at Steps? *Angew. Chem., Int. Ed.* **2010**, *49* (37), 6572−6575.

(23) Näslund, L.-Å. Hydrogenation of O and OH on Pt(111): A Comparison Between the Reaction Rates of the First and the Second Hydrogen Addition Steps. *J. Chem. Phys.* **2014**, *140* (10), 104701.

(24) Steininger, H.; Lehwald, S.; Ibach, H. Adsorption of Oxygen on Pt(111). *Surf. Sci.* **1982**, *123* (1), 1−17.

(25) Gland, J. L.; Sexton, B. A.; Fisher, G. B. Oxygen Interactions with the Pt(111) Surface. *Surf. Sci.* **1980**, *95* (2), 587−602.

(26) Williams, M. D.; Bethune, D. S.; Luntz, A. C. Coexistence of Precursor and Direct Dynamics: The Sticking of O_2 on a Pt(111) surface. *J. Chem. Phys.* **1988**, *88* (4), 2843−2945.

(27) Jacobse, L.; den Dunnen, A.; Juurlink, L. B. F. The Molecular Dynamics of Adsorption and Dissociation of O_2 on Pt(553). *J. Chem. Phys.* **2015**, *143* (1), 14703.

(28) Groß, A. Ab Initio Molecular Dynamics Simulations of the O_2/Pt(111) Interaction. *Catal. Today* **2016**, *260*, 60−65.

(29) Reuss, G.; Disteldorf, W.; Gamer, A. O.; Hilt, A. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(30) Krick Calderón, S.; Grabau, M.; Óvári, L.; Kress, B.; Steinrück, H. P.; Papp, C. CO Oxidation on Pt(111) at Near Ambient Pressures. *J. Chem. Phys.* **2016**, *144* (4), 44706.

(31) Silbaugh, T. L.; Karp, E. M.; Campbell, C. T. Energetics of Methanol and Formic Acid Oxidation on Pt(111): Mechanistic Insights from Adsorption Calorimetry. *Surf. Sci.* **2016**, *650*, 140−143.

(32) Campbell, C. T.; Ertl, G.; Kuipers, H.; Segner, J. A Molecular Beam Study of the Catalytic Oxidation of CO on a Pt(111) Surface. *J. Chem. Phys.* **1980**, *73* (111), 5862−5873.

(33) Willbourn, A. H.; Hinshelwood, C. N. The Mechanism of the Hydrogen-Oxygen Reaction. I. The Third Explosion Limit. *Proc. R. Soc. London, Ser. A* **1946**, *185* (1003), 353−369.

(34) Yaws, C. L. Matheson Gas Products. *Gas Data Book*, 7th ed.; McGraw-Hill Professional: New York, 2001.

(35) Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. How Well Does Pt(211) Represent Pt[n (111) × (100)] Surfaces in Adsorption/Desorption? *J. Phys. Chem. C* **2015**, *119* (24), 13551−13560.

(36) Tollens, B. Ueber ammon-alkalische Silberlösung als Reagens auf Formaldehyd. *Ber. Dtsch. Chem. Ges.* **1882**, *15* (2), 1828−1830.

(37) Tollens, B. Ueber ammon-alkalische Silberlösung als Reagens auf Aldehyd. *Ber. Dtsch. Chem. Ges.* **1882**, *15* (2), 1635−1639.

(38) Miller, A. V.; Kaichev, V. V.; Prosvirin, I. P.; Bukhtiyarov, V. I. Mechanistic Study of Methanol Decomposition and Oxidation on Pt(111). *J. Phys. Chem. C* **2013**, *117* (16), 8189−8197.