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Gaseous and Particulate Emissions from a Chimneyless Biomass Cookstove Equipped with a Potassium Catalyst

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Abstract

Approximately three billion people cook with solid fuels, mostly wood, on open fires or rudimentary stoves. These traditional cooking methods produce particulate matter and carbon monoxide known to cause significant respiratory health problems, especially among women and children, who often have the highest exposure. In this work, an inexpensive potassium-based catalyst was incorporated in a chimneyless biomass cookstove to reduce harmful emissions through catalytic oxidation. Potassium titanate was identified as an effective and stable oxidation catalyst capable of oxidizing particulate matter and carbon monoxide. Using a cordierite monolith to incorporate potassium titanate within a bespoke, rocket-style, improved cookstove led to a 36% reduction in particulate matter emissions relative to a baseline stove with a blank monolith and a 26% reduction relative to a stove with no monolith. Additionally, the catalytic stove reduced particulate matter emissions by 82%, reduced carbon monoxide emissions by 70%, and improved efficiency by 100% compared to a carefully tended, three-stone fire. Potassium titanate was also shown to oxidize carbon monoxide at temperatures as low as 500 °C, or as low as 300 °C when doped with copper or cobalt.

Graphical Abstract

Keywords

soot oxidation; potassium catalyst; indoor air quality; biomass; wood stove

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1. Introduction

Emissions produced by biomass cookstoves adversely affect indoor/local air quality, individual health, and global climate change. Biomass cookstoves often lead to high concentrations of particulate matter (PM) and other pollutants, which are estimated to be responsible for 1.6 million deaths annually, accounting for about three percent of the global disease burden [1]. Indoor air pollutants disproportionately affect women and children, and directly lead to an increase in chronic bronchitis, respiratory infections, and pneumonia [1]. In Guatemala, where field trials for our catalytic cookstove were recently completed, respiratory diseases are the leading cause of death [2]. Homes that use traditional cookstoves and open fires often exceed emissions (carbon monoxide [CO] and PM) limits established by the World Health Organization (WHO) by a factor of 10–20 [1].

The use of improved cookstoves to reduce emissions and the effect on indoor air quality has been studied extensively since 1968. Smith et al. [3] compared indoor air pollution levels collected across 250 communities and 71 studies published between 1968 and 2002. Much of the early work demonstrated that small changes to the design can significantly reduce emissions. For example, Boy et al. [4] found that adding an internal baffle to plancha stoves significantly improved thermal efficiency, and McCracken et al. [5] found a strong correlation between CO and PM_{2.5} concentrations in an average kitchen. Albalak et al. [6] saw an 85% reduction in PM_{3.5} by replacing an open fire with a plancha stove. Similar research conducted in India by Changappa et al. [7] and Dutta et al. [8] has shown that implementing improved cookstoves lowers CO emissions by up to 70% and PM_{2.5} emissions (PM with a diameter less than 2.5 micrometers) by 48%. However, Sinton et al. [9], after demonstrating similar results, noted that most households still have twice the recommended level of PM₁₀ despite introducing an improved cookstove.

Improved cookstoves typically fall into three categories: gasifier stoves, rocket stoves, and forced-air stoves. MacCarty et al. [10] found that forced-air stoves produce the least amount of CO emissions, followed by rocket stoves and then gasifier stoves. Similarly, they found that forced-air stoves produce the least amount of PM emissions, followed by gasifier stoves and then rocket stoves. Although forced-air stoves provide the best performance, they require electric power to operate. This suggests that a passive rocket-style stove could compete with forced-air stoves if its PM emissions could be further reduced.

Rocket stoves—small stoves with an insulated L-shaped combustion chamber—have undergone years of design and development focused on lowering CO and PM emissions. Analogous to the introduction of automobile emissions controls in the 1970s, rocket stoves have progressed to the point where further mechanical design changes are expected to have minimal effect on emissions. A chemical, rather than a mechanical change, is required, such as the introduction of an oxidation catalyst. In fact, several companies currently sell wood fired furnaces with noble metal catalysts located in the chimney for the U.S. residential market. However, common noble metal oxidation catalysts, such as platinum [11] and palladium [12], are prohibitively expensive for cookstoves intended for users living in or near poverty. Additionally, incorporating a catalyst in a chimneyless stove can be difficult.

Stove draft is proportional to exhaust stack height (i.e., a long chimney provides a greater draft). Therefore any obstructions (e.g., a catalyst) in the stove can drastically inhibit the buoyancy-driven air flow through the stove. Additionally, direct contact with flames can damage the catalyst. Recent studies into oxidation catalysts to reduce diesel engine soot emissions identified various metals (e.g., manganese [13], potassium [14], iron [15], etc.) as being effective oxidation catalysts, as well as more complex catalysts such as $\text{Mn}_{1.9}\text{M}_{0.1}\text{O}_{3-\delta}$ [16] and $\text{CoO}_x/\text{Sn-CeO}_2$ [17]. In this work, the activity and stability of 13 different metal oxide catalysts were assessed, the most promising catalyst was identified, and the advantages of integrating an inexpensive oxidation catalyst within a chimneyless rocket stove was demonstrated.

2. Experimental

2.1. Catalyst synthesis

Initially, eight catalysts were prepared for activity testing. Platinum black was purchased from Sigma Aldrich (PN# 205915), three manganese oxide catalysts (MnO , Mn_2O_3 , and Mn_3O_4) were purchased from Sigma Aldrich (PN# 431761, 463701, and 377473), and four potassium-based catalysts were synthesized. Potassium titanate ($\text{K}_2\text{Ti}_2\text{O}_5$) was prepared by grinding titanium dioxide and potassium carbonate together and calcining at 850 °C for 4 hours [18]. Potassium-calcium-silica glass at a 35:13:52 mass ratio was synthesized by dry-mixing potassium carbonate, calcium carbonate, and silicon dioxide and calcining the mixture at 1100 °C for 2 hours [19]. Two strontium potassium titanate catalysts ($\text{Sr}_{0.8}\text{K}_{0.2}\text{TiO}_3$ [20] and K-SrTiO_3 [21]) were also synthesized. $\text{Sr}_{0.8}\text{K}_{0.2}\text{TiO}_3$ was prepared via incipient wetness impregnation of titanium dioxide by using a solution of strontium nitrate and potassium nitrate in water followed by calcination at 550 °C for 2 hours and 800 °C for 4 hours. K-SrTiO_3 was prepared via incipient wetness impregnation of strontium titanate with a potassium nitrate solution and then calcined at 850 °C for 6 hours.

Additionally, six potassium-based catalysts were doped with copper, cobalt, or cerium in an attempt to enhance catalyst activity. $\text{K}_2\text{Ti}_2\text{O}_5$ was doped with cobalt, copper, or cerium by using the corresponding nitrate salts and incipient wetness impregnation to produce 5 wt% metal- $\text{K}_2\text{Ti}_2\text{O}_5$; the catalysts were calcined at 850 °C for 6 hours [22]. A cerium oxide-based catalyst (K-Co-CeO_2) was produced by incipient wetness impregnation using cerium oxide, cobalt acetate, and potassium carbonate and calcined at 850 °C for 12 hours [23]. A potassium copper oxide catalyst (K-CuO) was synthesized via incipient wetness impregnation of copper oxide with potassium carbonate and calcined at 350 °C for 4 hours [24]. Potassium cobalt oxide ($\text{K}_{0.25}\text{CoO}_2$) was synthesized by dry mixing potassium carbonate and cobalt(II,III) oxide and calcining at 850 °C for 12 hours [25].

2.2. Soot oxidation testing

Thermogravimetric analysis (TGA), performed with a TA Instruments Q600, was used to evaluate catalysts for soot oxidation activity. Catalysts were loosely mixed with carbon black powder (Cabot: Vulcan XC72R) as a soot simulant at a 10-to-1 ratio of catalyst to carbon black and loaded in the TGA. Carbon black, an elemental carbon, was used as the simulant because similar wood-burning rocket stoves have been shown to produce PM containing

80% elemental carbon and only 20% organic carbon [26], as a fraction of the total carbon. In contrast, open burning of wood generates PM containing 70%–80% organic carbon [27]. In keeping with the literature, the carbon mass was kept low to avoid heat and mass transfer limitations [28]. Carbon and catalyst were loosely mixed in a 20 mL vial, using a metal spatula, to better simulate the interaction between catalyst and soot within a cookstove. Air was flown through the TGA at 100 mL/min, and the temperature was increased by 10 °C/min until reaching 800 °C. Uncatalyzed soot oxidation was characterized by loading approximately 2 mg of carbon black in the TGA and using the same experimental conditions as the catalytic experiments. Mass loss data were collected as a function of time and analyzed using TA Universal Analysis software provided with the instrument. From the data, two key parameters were determined: ignition temperature (T_{ig}) and 50% mass loss temperature (T_{50}). Here T_{ig} is defined as the temperature where a line extrapolated from the initial mass (normalized mass =1) intersects a line drawn tangent to the inflection point of the mass loss curve, and is lower than T_{50} .

2.3. Catalyst stability

Catalyst stability was determined using the same TGA conditions used to measure catalyst activity. Stability tests were carried out by mixing 670 mg of catalyst with 67 mg of carbon in a 20 mL vial. Then 10 mg of the mixture was transferred to a 90 μ L sample cup, which was placed in the TGA furnace. After being run through the TGA furnace, only the catalyst remained in the 90 μ L sample cup. In order to reuse this catalyst sample, approximately 1 mg of carbon was added to the 90 μ L sample cup and mixed with the once-used catalyst. Each catalyst was tested in this manner for up to 25 runs. T_{ig} and T_{50} were determined for each run to determine any loss of catalyst activity.

A second, more time-intensive, stability test was also used to ensure the catalyst-carbon mixing technique was not influencing results. As before, 670 mg of $K_2Ti_2O_5$ and 67 mg of carbon were mixed together. 10 mg of the mixture was run through the TGA to determine the T_{ig} of fresh $K_2Ti_2O_5$. The remaining $K_2Ti_2O_5$ -carbon mixture (~740 mg) was placed in a muffle furnace and held at 800 °C for 1 hour. The catalyst removed from the muffle furnace (once-used $K_2Ti_2O_5$) was weighed and then mixed with fresh carbon black. Ten milligrams of the once-used $K_2Ti_2O_5$ -carbon mixture was tested with the TGA to determine the T_{ig} of once-used $K_2Ti_2O_5$. As before, the once-used $K_2Ti_2O_5$ -carbon mixture was placed in a muffle furnace to burn off the carbon and produce twice-used $K_2Ti_2O_5$. This process was repeated seven times. This second method avoided errors associated with mixing small quantities of material and more closely replicated the procedure used for the initial catalyst screening study.

2.4. Catalyst elemental characterization

Energy-dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition of freshly made catalysts and catalysts that had been used in soot oxidation experiments. EDS experiments were performed using an Amray 1845 Schottky field emission scanning electron microscope (SEM) equipped with an iXRF EDS. From the EDS measurements, the mass percent of each element present in a catalyst was determined. By

comparing freshly made catalysts to used catalysts, any changes in elemental composition that could lead to catalyst deactivation could be determined.

2.5. Carbon monoxide oxidation testing

In addition to soot oxidation activity, catalyst activity toward CO oxidation was also determined. CO oxidation activity was determined using a small flow reactor built from metal tubing. Stainless steel tubing with a 0.375 in. (0.952 cm) OD, 0.277 in. (0.704 cm) ID, and 6.0 in. (15.2 cm) length was packed with approximately 3.2 g of cordierite pieces coated with 10 wt% catalyst and plugged at each end with quartz wool. The coated cordierite pieces were randomly shaped and approximately 0.2 in. (0.5 cm) in size. The reactor was heated using heating tape, wrapped in insulation, and controlled using a proportional–integral–derivative (PID) controller. Dry air was flown through the reactor at 1.25 L/min, and the reactor temperature was held at 200 °C for 30 minutes to fully dry the catalyst. After 30 minutes, the flow of dry air was replaced with a gas mixture of 100 ppm by volume CO in air flowing at 1.25 L/min, corresponding to a gas hourly space velocity (GHSV) of 12,600 h⁻¹ (calculated based on reactor volume and at standard conditions). The reactor temperature was then increased in increments of 100 °C (up to 700 °C) and held at each temperature for 10 minutes. Effluent leaving the reactor was flown through a California Analytical Instruments non-dispersive infrared gas analyzer (Model 602) to determine CO and carbon dioxide (CO₂) concentrations.

2.6. Catalyst Deposition on the Monolith

Cordierite monoliths, purchased from Applied Ceramics Inc., were used as catalyst supports. Monoliths were 5.4 inches (13.6 cm) in diameter and contained 20 cells per square inch (CPSI). Monoliths were coated by using the washcoat method. Briefly, a slurry containing water, titanium dioxide, and potassium carbonate was created. The solid mass percent was varied to control the amount of catalyst deposited on the monolith. The slurry was mixed using a homogenizer to ensure uniformity. The monolith was then dipped in the slurry, making sure the monolith was fully submerged. The monolith was removed from the slurry, and compressed air was used to blow any excess liquid out of the monolith pores. The monolith was dried at room temperature for a minimum of 16 hours and then was calcined at 850 °C for 4 hours and allowed to cool to room temperature.

2.7. Cookstove testing and characterization

Four different stove configurations were tested: 1) an empty stove, 2) a stove incorporating a 0.5 inch (1.2 cm) blank monolith, 3) a stove incorporating a 0.5 inch K₂Ti₂O₅-coated monolith, and 4) a stove with a restricted fuel/air inlet and incorporating a 0.5 inch K₂Ti₂O₅-coated monolith. The stove was 14.25 inches (36.2 cm) tall and had a 10 inch (25.4 cm) diameter. The underside of the monolith was suspended 8.25 inches (21.0 cm) from the base of the stove using three angle brackets; further details can be found in the Supplementary Information. Each stove configuration was characterized using the Water Boiling Test (WBT) protocol version 4.2.2 [29], which measures the thermal efficiency and quantity of emissions produced by a stove during a simulated cooking process. The WBT provides a standard to compare stove performance in a controlled environment because real-world cooking processes are highly variable. The WBT consists of three different stages (cold start,

hot start, and simmer phase) that approximate different cooking phases. Each WBT involved measuring stove emissions, heat addition to the water, and fuel consumption. Starting with a cold stove and 5 liters of water in an aluminum pot, a fire was lit and maintained to bring the water to its boiling temperature. Immediately following the cold start, the fire was extinguished, fresh water was placed in the pot, and a new fire was kindled. The new pot of water was once again brought to a boil, ending the hot-start phase of the WBT. When the hot start was finished, the pot of water was held within 6 °C of the boiling temperature for a total of 45 minutes; this stage of the WBT was considered the simmer phase.

The aluminum pot used during the WBT was 7 inches (17.8 cm) tall, 9 inches (22.9 cm) in diameter, and weighed 600 grams. A thermocouple was positioned in the center of the pot and held approximately 2 inches (5 cm) from the pot bottom. Thermocouples were also placed in the stove to measure specific internal temperatures, including from bottom to top: in the fire, below the monolith, above the monolith, and below the pot. Similarly, a sampling probe was located above the monolith and connected to a Servomex 5200 multipurpose analyzer to measure oxygen (O₂) concentration within the stove to determine the excess air. The water, fire-starting materials, firewood, and remaining char were massed at the beginning and end of each phase. During each WBT, the same aluminum pot, stove operator, and type of firewood were used. Dimensional pine wood, 18 inches (45.7 cm) long and 0.7 inches (1.75 cm) thick with a square cross-section, was used for each WBT. Moisture content of the fuel was measured using a wood moisture meter (model # MMD8P) purchased from General Tools & Instruments; fuel moisture was typically 9%–11%.

The cookstove test stand followed the specifications outlined in the WBT and is shown in Figure 1. A dedicated hood and exhaust system, incorporating 6 inch (15.2 cm) ducting, was installed to collect and direct stove emissions to several pieces of analytical equipment. The hood was located 36 inches (91.4 cm) above the cookstove. A blower maintained the flow rate through the exhaust duct at approximately 190 m³/hr, as measured by an orifice plate and differential pressure gauge. A set of mixing baffles after the hood inlet ensured a well-mixed emissions sample. A sample probe (leading to the analytical equipment) was located 24 inches (61 cm) upstream of the blower and 60 inches (152 cm) downstream of the mixing baffles. The sample line led directly to analyzers for CO, CO₂, particulate number (PN), nitrogen oxides (NO_x), and total hydrocarbons (THC) concentrations. The sample line also included a cyclone (URG Corporation, model 2000-30ED) to exclude coarse particles greater than approximately 2.5 μm. CO and CO₂ concentrations were measured using a California Analytical Instruments 602 series non-dispersive infrared analyzer. THC concentration was measured using a flame ionization detector analyzer (Thermo Scientific Model 51i-HT). A Thermo Scientific model 42i-HL analyzer measured NO_x concentrations. PN concentrations were measured with a TSI 3775 condensation particle counter (CPC). The CPC had a lower detection limit of 4 nm particles and could detect particles > 3 μm (superseded by the 2.5 μm cyclone cutoff). The sample probe for the CPC was designed to be nearly isokinetic, and the stainless steel sample lines were kept short, less than 70 inches (177.8 cm), to minimize sample line losses. Sample flow rate to the gas analyzers was set by a choked critical orifice backed by a diaphragm vacuum pump. The sample flow rate to the CPC was set by internal instrument pumps. The dilution of the stove exhaust with room air pulled through the hood was sufficient such that additional dilution of the sample was not

required before reaching the instruments, with the exception of the CPC, which was diluted with an additional 1.38 L/min of dry, filtered air. PM concentrations were measured with a Pegasor PPS M analyzer. The Pegasor had an internal cyclone that excluded particles $> 1 \mu\text{m}$ and restricted the maximum detectable particle size to $1 \mu\text{m}$. Previous research by Shen et al. [30] has shown that soot particles from a wood-fired stove are well under $1 \mu\text{m}$ in diameter, and therefore, the PM mass measured by the Pegasor should be directly comparable to the PN measured by the CPC. The Pegasor included its own heated sample lines, with an inlet and outlet separated by 2.95 inches (7.5 cm). The Pegasor inlet was located 19 inches (48.3 cm) upstream of the blower.

3. Results and Discussion

3.1. Metal oxide soot oxidation activity

TGA results in Figure 2 show the weight loss curve of carbon black alone and in the presence of eight different oxidation catalysts, including potassium, manganese, and platinum catalysts. These catalysts were chosen because potassium [28] and manganese [13] are inexpensive elements previously shown to catalyze oxidation, while platinum is a commercial, but expensive oxidation catalyst. The mass of carbon black in each experiment was normalized on a scale of zero (all carbon is consumed) to one (no carbon is consumed) and is plotted as a function of temperature. Figure 2 shows that the most effective catalysts were K-Ca-Si glass, $\text{K}_2\text{Ti}_2\text{O}_5$, and $\text{Sr}_{0.8}\text{K}_{0.2}\text{TiO}_3$ because each catalyst shifts the carbon black weight loss curve to the left of uncatalyzed carbon oxidation. Of the three promising catalysts, it is noteworthy that the K-Ca-Si glass catalyst curve has two different slopes, an initial steep decline associated with carbon decomposition followed by a shallow decline that could be explained by decomposition of the catalyst itself, which was supported by subsequent stability testing. TGA results were also used to calculate the ignition temperature (T_{ig}) and the 50% weight loss temperature (T_{50}) for each catalyst (Table 1). The data show that T_{ig} was decreased by 100°C and T_{50} was decreased by 95°C when using the most effective catalysts. Previous studies using the same catalysts have shown a wide range in T_{ig} depending on the experimental conditions. For example, Su et al. [31] mixed K-Ca-Si glass catalyst with soot using a wet-deposition method to produce tight catalyst-soot contact and observed T_{ig} between 380°C and 470°C , while we observed T_{ig} of 535°C using loose contact between K-Ca-Si glass and carbon black. In a follow on study, Su et al. [28] deposited soot (from a flame or a diesel engine) on a K-Ca-Si glass surface and found that tight contact produced T_{ig} of 360°C and loose contact produced T_{ig} of 423°C . Similarly, Meng et al. [18] and Ura et al. [32] determined catalyst activity by measuring CO_2 production, which cannot be directly compared to TGA mass-loss measurements conducted here and elsewhere.

In addition to several potassium catalysts, three manganese oxide catalysts were also tested for carbon oxidation activity. Mn_2O_3 and Mn_3O_4 both displayed carbon oxidation activity, but reduced T_{ig} by only 36°C and 19°C , respectively. MnO demonstrated no carbon oxidation activity and actually showed a small increase in sample mass during testing. This was most likely caused by oxidation of MnO to MnO_2 . Wagloehner et al. [33] previously observed that Mn_2O_3 and Mn_3O_4 (held in tight contact with soot) can reduce soot oxidation

temperature by nearly 250 °C, further demonstrating that soot oxidation temperatures are highly dependent on experimental technique.

A high-cost platinum catalyst was also tested as a comparison to the low-cost potassium and manganese oxides investigated here. Platinum black shows a T_{ig} of 425 °C, which is significantly lower than the best potassium oxide catalysts. However, at these low temperatures, oxidation is incomplete. Figure 2 shows that the Pt-black mass loss curve flattens between 475 and 575 °C, resulting in a second T_{ig} at 594 °C and a T_{50} at 605 °C. Two possible causes may have produced the unusual Pt-black weight loss curve. First, only a small portion of the carbon was in good contact with the Pt-black catalyst, and platinum promoted oxidation of the bulk carbon black only at higher temperatures. Second, the platinum catalyst suffered sulfur poisoning as carbon black was oxidized; evidence of sulfur poisoning was observed via EDS elemental analysis (see Supplementary Information). Carbon black typically contains 0.1–1.0 wt% sulfur [34], while woody biomass typically contains 0.04 wt% sulfur [35]; therefore, sulfur poisoning is expected to be minimal during cookstove operation.

3.2. Doping potassium oxide catalysts with transition state metals

Evidence in the literature suggests that doping potassium oxide catalysts with certain metals can improve activity toward soot oxidation. Wang et al. [22] found that doping $K_2Ti_2O_5$ with copper, cobalt, or cerium can lower soot oxidation temperatures when in the presence of NO. Lopez-Suarez et al. [21] observed that adding copper to $K/SrTiO_3$ catalysts can improve soot oxidation activity, while Jakubek et al. [25] showed that combining potassium and cobalt ($K_{0.25}CoO_2$) further enhances soot oxidation activity.

The TGA results of six potassium oxide catalysts doped with copper, cobalt, or cerium are shown in Figure 3 and the calculated T_{ig} and T_{50} for each catalyst is shown in Table 2. Both K-Co-CeO₂ and K-CuO catalysts improved oxidation activity compared to the uncatalyzed case but were not as effective as undoped $K_2Ti_2O_5$. However, doping $K_2Ti_2O_5$ with 5 wt% copper, cobalt, or cerium improved the T_{ig} by 17–32 °C and the T_{50} by 47–56 °C when compared to $K_2Ti_2O_5$. Similarly, $K_{0.25}CoO_2$ improved the T_{ig} and T_{50} by 16 and 36 °C, respectively, compared to $K_2Ti_2O_5$.

3.3. Catalyst stability

Stewart et al. [36] and Taylor III et al. [37] have found previously distributed stoves last 3 to 4 years, while newly developed stoves are expected to last more than 5 years [38]; it is important the catalyst remains active over the lifetime of a cookstove. The seven most effective catalysts were tested for stability by reusing a specific catalyst sample up to 25 times. The results of one specific catalyst ($K_2Ti_2O_5$) are shown in Figure 4A where T_{ig} is plotted against experiment run number. Figure 4A shows an initial spike in T_{ig} of 50 °C between experiment one and two, after which T_{ig} remains relatively constant with an average of 587 °C.

The step change in T_{ig} from 525 °C to 587 °C after the first run could indicate an initial loss in activity. However, the increase could also be a result of the experimental method. Work by Meng et al. [18] and Su et al. [28] has shown that the extent of contact between a catalyst

and carbon can affect T_{ig} by up to 50 °C, which suggests that mixture preparation could affect the results of stability testing. The first round of stability tests used a different mixing method for run number one, and all subsequent runs. Initially, catalyst (~670 mg) was mixed with carbon (~67 mg) in a 20 mL vial and then 10 mg of the sample was run through the TGA. After the initial TGA run, ~9 mg of catalyst remained in the 90 μ L sample cup. In order to reuse this catalyst sample, ~1 mg of carbon was added to the 90 μ L sample cup and mixed with the once-used catalyst. This technique resulted in different extents of mixing between the first data point in Figure 4A and all subsequent data points. These two different extents of mixing could therefore account for the apparent loss in $K_2Ti_2O_5$ activity between runs one and two seen in Figure 4A. In order to confirm this supposition, we used a different experimental method (Section 2.3) that utilized larger sample sizes throughout the experiment. The results of this second stability testing method are shown in Figure 4B, which shows that after several uses, $K_2Ti_2O_5$ T_{ig} averaged 487 °C. This confirms that $K_2Ti_2O_5$ does not lose activity upon repeated use and that any apparent loss of activity shown in Figure 4A was the result of incomplete catalyst-carbon mixing.

While the second stability testing method was more accurate, it was also time consuming. Therefore, we screened each catalyst for stability using the first screening method to rapidly evaluate catalyst stability. In addition to $K_2Ti_2O_5$, $K_{0.25}CoO_2$ and 5 wt% Cu- $K_2Ti_2O_5$ were found to be stable with an average T_{ig} of 580 °C and 574 °C, respectively. In contrast, K-Ca-Si glass and $Sr_{0.8}K_{0.2}TiO_3$ were unstable. $Sr_{0.8}K_{0.2}TiO_3$ lost all activity after one run, while K-Ca-Si glass deactivated over the course of eight runs. Similar results were observed by Lopez-Suarez et al. [21] showing $Sr_{0.8}K_{0.2}TiO_3$ deactivates after one use and Su et al. [28] showing K-Ca-Si glass begins to deactivate when heated above 600 °C. Stability plots for these catalysts can be found in the Supplementary Information.

Each catalyst was also examined using SEM and EDS to determine why certain catalysts deactivated after repeated use. The resulting data is shown in Table 3 where the weight percent of potassium is reported for fresh and used catalysts. Freshly made catalysts and used catalysts were put through as many as 25 TGA reaction cycles. Unstable catalysts (K-Ca-Si glass and $Sr_{0.8}K_{0.2}TiO_3$) showed a sharp decrease in potassium after repeated use, which could explain the loss of activity. EDS linescans showed that potassium loss was not localized, which suggested that decreased potassium mass was caused by decomposition as opposed to sintering/agglomeration. Temperatures within the stove and near the catalytic monolith periodically reached 900 °C, which therefore eliminated K-Ca-Si glass and $Sr_{0.8}K_{0.2}TiO_3$ as potential cookstove catalysts. In contrast, $K_2Ti_2O_5$ and 5 wt% Cu- $K_2Ti_2O_5$ experienced negligible changes in potassium concentration and were both stable over a minimum of 25 runs. $K_{0.25}CoO_2$ experienced a potassium decrease of 46% but was still stable after 20 experiments. Based on EDS linescans (Supplementary Information), potassium appeared to sinter on the surface of $K_{0.25}CoO_2$ and form localized regions of potassium. Some EDS elemental scans showed no potassium present, while other scans showed potassium levels that were similar to the fresh catalyst. Since the EDS measurement only looks at a small portion of the catalyst surface, it is likely that rather than losing potassium, $K_{0.25}CoO_2$ formed agglomerates of potassium while retaining the same bulk elemental composition. Potassium sintering can reduce the number of potassium surface sites and eventually reduce the activity of the catalyst. Because these experiments used a

large catalyst-to-carbon ratio (10:1), this activity loss was unobserved. In a real world cookstove application with smaller potassium loading, $K_{0.25}CoO_2$ is unlikely to be an effective, long-term catalyst.

Additionally, every catalyst showed a non-negligible incorporation of sulfur after being used to oxidize carbon black (Supplementary Information). Typically, sulfur readily poisons reduced metal catalysts [39], while potassium oxide catalysts, such as $K_2Ti_2O_5$, are considered sulfur resistant [18]. Sulfur present in the carbon black used here did not deactivate $K_2Ti_2O_5$, $K_{0.25}CoO_2$, or 5 wt% Cu- $K_2Ti_2O_5$. However, whether K-Ca-Si glass or $Sr_{0.8}K_{0.2}TiO_3$ deactivated due to the presence of sulfur is unclear. Both K-Ca-Si glass [28] and $Sr_{0.8}K_{0.2}TiO_3$ [21] have been shown previously to deactivate at high temperatures, suggesting that elevated temperature and not sulfur led to catalyst deactivation. Nevertheless, sulfur cannot be definitively ruled out as the source of K-Ca-Si glass and $Sr_{0.8}K_{0.2}TiO_3$ deactivation.

Following the catalyst screening and stability studies, the most promising catalyst was identified for incorporation into a biomass cookstove. K-Ca-Si glass and $Sr_{0.8}K_{0.2}TiO_3$ were eliminated due to stability issues. $K_{0.25}CoO_2$ was eliminated despite its stability because potassium sintering was observed. Of the remaining catalysts, $K_2Ti_2O_5$ was chosen over 5 wt% Cu- $K_2Ti_2O_5$ because after repeated use, each catalyst had about the same average ignition temperature. Adding copper to the catalyst was not justified when no benefit to soot oxidation was apparent; however, a later set of experiments did uncover a benefit to CO oxidation as discussed in a subsequent section.

3.4. Incorporating a catalyst in a rocket stove

Creating a catalytic, biomass stove required a method to incorporate the powdery $K_2Ti_2O_5$ catalyst that was self-supporting within the stove. As an initial proof of concept, several ceramic support structures were placed in a simple rocket stove to ensure the stove was still operational. Air flow through the stove was buoyancy-driven and small changes to the flow resistance led to significant changes in emissions and thermal efficiency. Ceramic spheres with a 1-cm diameter greatly limited air flow through the stove and caused smoke to backflow out the stove inlet. Subsequently, several ceramic monoliths made of cordierite were also tested. We found that 5.4 inch (13.7 cm) diameter monoliths with a cell density of 20 CPSI allowed appropriate air flow for the stove to function properly.

Cordierite monoliths were chosen because cordierite has a low thermal expansion coefficient, high refractoriness, and good mechanical strength [40]. Cordierite also provides an excellent surface to adhere metal oxide catalysts because of its metal oxide formulation and its porosity. Coating monoliths is often carried out by deposition from a slurry of particles, referred to as washcoating [40]. The process entails dipping a monolith in catalyst-water slurry, followed by drying and calcination. Several parameters were investigated (Figure 5) to determine the ideal method of coating the monolith, including washcoat number, slurry solids weight percent, and solid particle size. As expected, increasing the number of washcoats or the slurry solids weight percent increased the amount of catalyst that adhered to the monolith (Figure 5). Each additional washcoat approximately doubled the mass of catalyst coated on a monolith, while increasing the slurry solids weight percent

by 10% approximately doubled the catalyst mass deposited on the monolith. Additionally, Figure 5A shows that using smaller solid particles in the washcoat slurry increased the mass of deposited catalyst. Similarly Nijhuis et al. [41] suggested using particles $<5\text{ }\mu\text{m}$, and Avila et al. [40] found that using smaller particles improved alumina adhesion to a monolith. Based on the washcoating results, monoliths were coated once using 25 wt% slurry made with 20 nm solid particles. The coated monoliths had an average catalyst loading of approximately 10% by mass.

3.5. The effect of a potassium oxide catalyst on rocket stove emissions

To determine the effect of using an oxidation catalyst, a bespoke rocket stove was built that could accept the catalyst. A picture and schematic of the stove can be found in the Supplementary Information. The stove was 15 inches (38.1 cm) tall and 10 inches (25.4 cm) in diameter. The stove chimney was circular with a 5.4 inch (13.7 cm) diameter to accommodate a monolith and tapered down to a 4.0 inch (10.2 cm) diameter near the chimney exit. The stove was built in two halves that were connected with a quick-release, duct clamp so that catalysts could be swapped out easily for testing. The rocket stove was tested initially without a monolith to gauge its performance relative to a traditional three-stone fire. Figure 6A shows the particulate matter emission rate at high and low power for a three-stone fire, the rocket stove, and the rocket stove equipped with a pot skirt (see Supplementary Information for visualization). A pot skirt is an attachment that extends up and around the pot, thereby increasing heat transfer and improving thermal efficiency. Three-stone fire baseline results were taken from the compilation of Jetter et al. [42]. Without using any catalyst, the simple rocket stove was able to reduce specific PM emissions by approximately 70% alone and by 80% when operated with a pot skirt attachment compared to the three-stone fire.

Using the same rocket stove, additional tests were conducted with a blank cordierite monolith and a $\text{K}_2\text{Ti}_2\text{O}_5$ -coated monolith. Figure 6B shows that regardless of the stove configuration, the total PN produced was on the order of 10^{14} particles. In terms of particulate mass, adding a blank monolith to the rocket stove increased PM emissions by 16%. The error bars on PM correspond to one standard deviation calculated from triplicate measurements. Adding a blank monolith to the stove also caused CO emissions to increase (see Supplementary Information). This increase in emissions is likely tied to a decrease in airflow through the stove. The oxygen concentration exiting the stove, and prior to dilution with room air, was measured to determine the percent excess air (EA), a measure of the air-fuel ratio in the combustion chamber. These measurements revealed that O_2 concentration decreased from approximately 19.8% (1800% EA) to 18.7% (850% EA) when a 0.5 inch (1.3 cm) blank monolith was introduced to the stove. O_2 was further reduced to 15.6% (290% EA) when a 1.0 inch (2.5 cm) blank monolith was introduced to the stove. With less airflow passing through the stove, the stove temperature increased because the combustible mixture was less fuel lean; this trend was observed with 0.5, 1.0, and 1.5 inch monoliths (see Supplementary Information). This change in stoichiometric air-fuel ratio and temperature must have pushed the stove into a less clean-burning regime.

Although adding a blank monolith to the stove increased PM emissions, coating that same monolith with $K_2Ti_2O_5$ reduced PM emissions by 25% compared to a blank monolith and 12% compared to an empty stove. The catalytic effect of $K_2Ti_2O_5$ within the stove was large enough to overcome any increase in PM emissions caused by monolith introduction. This decrease in PM corresponded to a small increase in PN (Supplementary Information), suggesting that the catalyst may convert large soot particles to gas as well as several smaller particles. Similar results have been observed by Shen et al. [30], finding that a stove can reduce $PM_{2.5}$ mass without decreasing PN concentration and that the type of stove/fuel can significantly affect the average soot particle size. Toxicological research suggests that in addition to PM mass concentration, PN concentration and chemical composition also affect human health risks [43]. Therefore, the lack of a correlation between PM and PN found in this study leads us to recommend that future improved cookstove studies should measure both PM and size-resolved PN emissions to better understand the benefits of adopting improved cookstoves.

In addition, adding $K_2Ti_2O_5$ to the monolith reduced CO emissions compared to the blank monolith, suggesting that $K_2Ti_2O_5$ oxidizes CO. However, the CO reduction was insufficient to match CO levels from an empty stove (i.e., a stove not containing a catalyst monolith). Why $K_2Ti_2O_5$ was able to decrease PM emissions compared to an empty stove, but was unable to do the same for CO emissions is unclear. While $K_2Ti_2O_5$ is active for CO oxidation, possibly $K_2Ti_2O_5$ CO oxidation activity is insufficient to account for the decrease in excess air caused by introducing the monolith. A second possibility is that partial oxidation of soot, promoted by $K_2Ti_2O_5$, generates additional CO. Although $K_2Ti_2O_5$ is effective at oxidizing soot to gaseous species, that oxidation might be incomplete such that CO is produced alongside CO_2 . In such a case, as soot is oxidized to CO and CO_2 , $K_2Ti_2O_5$ may be unable to oxidize CO quickly enough to make up for increased CO production. While introducing the catalytic monolith increases CO emissions compared to an empty stove, doping $K_2Ti_2O_5$ with copper or cobalt could alleviate the increase in CO observed here. Section 3.6 describes how doping $K_2Ti_2O_5$ with copper or cobalt lowers the temperature at which CO begins to oxidize, which would help to lower CO emissions produced by the catalytic cookstove.

Emissions were improved further by decreasing the size of the fuel inlet and thereby restricting air flow into the stove; the restriction of air flow, combined with introducing a catalyst, reduced PM emissions by 36% compared to a stove incorporating a blank monolith and 26% compared to a stove with no monolith. Restricting air flow also decreased CO emissions by 30% compared to a stove incorporating a blank monolith. However, restricting air flow was unable to return CO emissions to the level of a stove with no monolith. Despite this, a follow-on field trial study [44] determined that the stove never exceeded 24-hour average (7 mg/m^3) or 15-minute acute (100 mg/m^3) CO limits set by WHO. Due to the complexity of the system, why restricting the fuel inlet decreased emissions when restricting airflow with a blank monolith increased emissions is unclear. However, restricting the fuel inlet demonstrated that further design optimization is needed to fully take advantage of $K_2Ti_2O_5$ oxidation activity. Incorporating the $K_2Ti_2O_5$ catalyst effectively shifted the objective function curve such that a new optimal configuration must be found to most effectively reduce PM and CO emissions.

Not only did a $K_2Ti_2O_5$ catalyst effectively reduce PM emissions in a cookstove, it also remained active during repeated testing. However, operating within a wood-fired cookstove has the potential to contaminate the $K_2Ti_2O_5$ catalyst with ash containing inorganics (Ca, Si, Mg, K, etc.) naturally present in wood and other biomass fuels. During biomass combustion, inorganic ash can deposit on solid surfaces and form a slag layer. This slag formation is believed to be initiated by condensation of KCl (and sometimes K_2SO_4), followed by other solid inorganics adhering to the condensed KCl [45]. The condensation temperatures of KCl and K_2SO_4 are 770 °C and 745 °C, respectively [45]. The average temperature of the catalytic monolith ranged between 420 °C and 590 °C, while maximum temperatures reached 900 °C. At these temperatures, inorganic ash could potentially deposit on the catalytic monolith. As confirmation, we used EDS to measure the elemental composition of a $K_2Ti_2O_5$ catalyst that was used in a wood-fired cookstove for more than ten real-world cooking events. EDS revealed that inorganic contamination was uneven. Two catalyst locations revealed no inorganic contamination, while two other locations revealed moderate levels (3–10 wt%) of Ca and low levels (1–3 wt%) of Mg and Si. Additionally, EDS revealed moderate potassium loss (approximately 10–20 wt%). Despite potassium loss and the presence of some inorganic fouling, we observed no decrease in the $K_2Ti_2O_5$ catalyst effectiveness.

3.6. Carbon monoxide oxidation

In addition to particulate matter, carbon monoxide also poses a health risk to people using indoor cooking fires. Initial results from stove testing suggest that introducing a monolith leads to an increase in CO emissions when compared to no monolith (Supplementary Information). Coating the same monolith with $K_2Ti_2O_5$ caused CO emissions to decrease compared to the blank monolith. However, CO levels remained higher than what was emitted from an empty stove. This result suggested that $K_2Ti_2O_5$ was catalytically active for CO oxidation. To confirm this, a known amount of CO in air (100 ppm, by mole) was flown through a small tubular reactor packed with catalyst. Figure 7 shows that uncoated cordierite was unable to promote CO oxidation. However, when cordierite was coated with $K_2Ti_2O_5$, CO was oxidized as low as 500 °C (4% conversion) with conversion reaching 45% at 700 °C. As suspected, this confirms that $K_2Ti_2O_5$ is catalytically active for CO oxidation. Average temperature of the monolith ranged from 452 °C to 652 °C depending on location and heating power. At lower temperatures the kinetics of CO oxidation are too slow to effectively mitigate CO production. Finding ways to increase the catalyst temperature, increase CO residence time within the catalyst, or inducing a more tortuous flow path could improve CO oxidation rates. However, making such changes could have an adverse effect on combustion efficiency and CO formation at the fuel source. Therefore, we decided a more effective solution was to improve catalyst activity by doping $K_2Ti_2O_5$ with additional elements.

Previous research has shown that doping $K_2Ti_2O_5$ can effectively improve oxidation rates. For example, Wang et al. [22] found that doping $K_2Ti_2O_5$ with cobalt promoted oxidation of NO to NO_2 . In an attempt to improve CO oxidation activity, $K_2Ti_2O_5$ was doped with several different metals, including cobalt, copper, and cerium. Figure 7 shows the results of doping $K_2Ti_2O_5$ with these metals. Cerium doping was largely ineffective since CO

conversion did not improve compared to pure $K_2Ti_2O_5$. However, copper and cobalt significantly lowered the temperature where CO oxidation began and improved the overall conversion of CO. After doping with either copper or cobalt, CO oxidation was observed as low as 300 °C (10–20% conversion), and by 700 °C CO conversion was approximately 90% for each metal doped catalyst. During stove operation, the average temperature of the catalyst ranged between 450 °C and 650 °C depending on location and stove firepower (Supplementary Information). Based on the packed bed CO reactor tests and average stove temperatures, CO conversion would range from 0–35% using a $K_2Ti_2O_5$ catalyst. Simply doping $K_2Ti_2O_5$ with either copper or cobalt could therefore reduce CO stove emissions by increasing CO conversion to between 55% and 90% at the same stove temperatures.

4. Conclusions

For the first time, an inexpensive catalyst was incorporated within a chimneyless cookstove to reduce harmful emissions. Potassium oxide catalysts incorporating a variety of elements were synthesized and examined for soot oxidation within biomass cookstoves. Via TGA testing, potassium titanate was found to be the most stable and active soot oxidation catalyst and was shown to promote catalytic oxidation of carbon monoxide to carbon dioxide. Additionally, doping potassium titanate with copper or cobalt further enhanced carbon monoxide oxidation activity. Upon introduction in a rocket-style cookstove, potassium titanate successfully reduced particulate matter emissions by 36% compared to an empty stove and by 82% compared to a carefully tended, three-stone fire. While introducing the catalyst increased carbon monoxide emissions compared to the same stove with no monolith present, carbon monoxide emissions were still below recommended limits. Particle number results suggested that potassium titanate partially oxidized soot particles without decreasing the total particle number and that future improved cookstove studies should incorporate size-resolved particle number measurements to better understand the health effects of improved cookstoves. Minor design modifications, such as restricting the fuel feed inlet, and catalyst optimization (e.g., doping with copper/cobalt) could be used to further reduce particulate matter and carbon monoxide emissions, suggesting that the catalytic rocket stove can be further optimized.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Potassium titanate was an effective catalyst for soot and carbon monoxide oxidation.
- Catalyst deactivation was caused by loss of potassium from the catalyst surface.
- Cookstove emissions were sensitive to small, draft-related design changes.
- Particulate matter emissions were reduced in standardized water boil tests.

Figure 1.
Experimental setup for testing biomass cookstoves.

Figure 2. Catalyst screening. Potassium and manganese catalysts were tested for soot oxidation activity using TGA.

Figure 3.
Metal-doped potassium-based catalyst screening.

Figure 4. Potassium titanate catalyst stability. A) Small scale stability testing using 10 mg of catalyst, B) large scale stability testing using 670 mg of catalyst.

Figure 5. Catalyst washcoating parameters. Ceramic monoliths were coated with $K_2Ti_2O_5$. A) The effect of washcoat number and catalyst particle size, and B) the effect of slurry mass percent.

Figure 6.

Particulate matter emissions produced by different stove configurations. A) Comparison of particulate matter produced from a three-stone fire (3SF) and a Mainstream stove with and without a pot skirt (PS) and B) Comparison of total particulate matter and total particulate number produced from a stove with no monolith and the same stove with a blank or catalytic 0.5 inch monolith.

Figure 7.
Carbon monoxide oxidation using potassium catalysts.

Table 1.

TGA Results of Catalyst Screening.

Catalyst	T_{ig} [°C]	T_{50} [°C]
No Catalyst	623	672
K-Ca-Si Glass	535	578
K ₂ Ti ₂ O ₅	525	588
K/SrTiO ₃	540	608
Sr _{0.8} K _{0.2} TiO ₃	524	594
MnO	636	677
Mn ₂ O ₃	587	646
Mn ₃ O ₄	604	652
Pt-Black	425 (594)	605

Table 2.

TGA Results of Metal-Doped Potassium-Based Catalyst Screening.

<i>Catalyst</i>	<i>T_{ig}</i> [°C]	<i>T₅₀</i> [°C]
No Catalyst	623	672
K ₂ Ti ₂ O ₅	525	588
5 wt% Ce/K ₂ Ti ₂ O ₅	493	532
5 wt% Cu/K ₂ Ti ₂ O ₅	499	541
5 wt% Co/K ₂ Ti ₂ O ₅	507	539
>K _{0.25} CoO ₂	508	552
K-CuO	560	595
K-Co-CeO ₂	608	653

Table 3.

Electron Dispersive Spectroscopy of Fresh and Used Catalysts

Catalyst	Potassium mass %, Fresh	Potassium mass %, Used	Potassium lost [%]
$\text{Sr}_{0.8}\text{K}_{0.2}\text{TiO}_3$	4.29	1.82	−57.6%
K-Ca-Si Glass	98.2	68.1	−30.6%
$\text{K}_2\text{Ti}_2\text{O}_5$	45.7	43.5	−4.89%
$\text{K}_{0.25}\text{CoO}_2$	13.0	6.98	−46.4%
5 wt% Cu/ $\text{K}_2\text{Ti}_2\text{O}_5$	39.3	42.2	+7.48%