ORIGINAL ARTICLE

Catalytic Oxidation of Carbon Monoxide from Vented Gas Space Heaters Using Alumina foam Supported CuMnOx Nanocatalyst

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Abstract

Background: Carbon monoxide (CO) is an odorless, tasteless, colorless, and nonirritating poisonous gas, recognized as the silent killer for the 21st century. It is produced during partial combustion of carbon-containing compounds. Improper ventilation and flue installation of vented gas space heaters cause carbon monoxide gas to penetrate the building, leading to many deaths annually. The catalytic oxidation of CO has received great attention due to its applications in different fields. In this study, alumina foam coated by CuMnOx catalyst was used to remove CO from the vented gas space heaters.

Methods: This is a full-scale experimental study on the outflow from vented gas space heaters. Alumina foam supported hopcalite (CuMnOx) catalyst was synthesized using a co-precipitation method for CO oxidation from the vented gas space heaters. The XRD and SEM were used to characterize the synthesized catalyst. The concentration of CO was measured by IMR 1500 combustion gas analyzer.

Results: The particle size of the catalyst was in the range of 200-600 nm. XRD showed different crystallizations, and the crystal size was in the range of 20-120 nm. There was no significant CO removal in the case of using uncoated alumina foam. Results showed CuMnOx catalyst significantly increased the CO removal. The removal efficiencies were 83% and 89% in heating powers of 2300 and 3200 kcal/hr, respectively. The average CO conversation rate was approximately 60.45 µg/gr.min.

Conclusion: CuMnOx coated on alumina has a significant effect on CO removal from the vented gas space heaters. The catalyst and outlet gas temperature were the most important factors affecting CO removal.

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Keywords: Carbon monoxide, Hopcalite, Air pollution, Indoor

Introduction

Carbon monoxide (CO) is a toxic gas, especially to human beings, due to its reaction with hemoglobin to form carboxyhemoglobin (COHb).[1] It is an odorless, colorless, tasteless and non-irritating gas, which makes it difficult for humans to detect and does not give a clear warning to its victims that they are at risk.[2] Nowadays, it is one of the most common poisons in our indoor environment and a leading cause of thousands of deaths every year worldwide.[3] CO is a product of partial combustion of carbon-containing compounds. Inhaling even relatively tiny amounts of CO can lead to hypoxic damage and neurological injury.[4] Large amounts of CO

in the world are mainly emitted from transportations, power plants, and manufacturing and domestic activities. It was estimated that automobile exhaust is the largest source of CO pollution in developed countries.[5]

Many epidemiologic studies attempted to link the concentration of environmental pollutants to population health problems. However, many of these studies focus on the outdoor environment even though people spend approximately 90 percent of their time indoors.[6, 7]

Indoor sources of CO are mostly combustion sources (cooking and heating) and its infiltration from outdoor. Incomplete oxidation during combustion causes a high concentration of indoor carbon monoxide.[8] In developed countries, the most important sources of exposure to this pollutant are incomplete combustion gas emissions, improper installation, poor maintenance or poor ventilation of cooking and heating equipment burning fossil fuels. Blocked flues, wood combustion fireplaces, decorative fireplaces, gas burners and heaters without proper safe operation can emit indoor CO.[9]

Due to easy access to natural gas in Iran, heating system in many homes uses vented gas space heaters which generate heat by burning natural gas.[10] Despite the change of heating systems from traditional heaters to central packages, Oxygen Depletion Sensor (ODS) system and, non-flue heaters, carbon monoxide is still produced from incomplete gas combustion. It has been reported that carbon monoxide poisoning led to 749 deaths in Iran in 2018.[11]

Catalytic CO oxidation is a famous process in the industry. Treatment of exhaust gases from internal combustion engines, excretion of petrochemical and metallurgical gases, production of pure gases, and CO oxidation to produce pure hydrogen (without CO) in the proton exchange membrane of fuel cells are some applications of this technology in the industry.[12] One of the most widely studied heterogeneous catalytic reactions is the low-temperature CO oxidation process, which is used extensively to reduce emissions of car pollutants.[13]

Hepacalite (CuMnOx), mixed copper oxide (Cu) and manganese (Mn) are used as catalysts for CO oxidation. Compared to other catalysts, hepacalite is one of the oldest known catalysts for low-temperature CO oxidation.[4] Ceramic foams are widely used in the heterogeneous catalytic process; however, the use of foam-coated catalysts is under development for pollution abatement processes such as catalytic converters or conventional catalytic processes.[14]

The use of alumina coated with copper-manganese catalysts to remove carbon monoxide from the gaseous texture has been studied, but most of these studies have not been performed under the real circumstance and the effect of natural conditions on the catalytic performance of this compound has not been investigated.[15-17] According to Krasimir et al., the active component of the mixed Cu- Mn/γ–alumina catalysts strongly depends on the Cu/Mn molar ratio. Highly activated alumina supported Cu-Mn catalysts for oxidizing CO, methanol and dimethyl ether were synthesized. They reported that the hopcalite catalyst is highly efficient for CO oxidation and the best compromise for simultaneous oxidation of all gaseous pollutants was the catalyst with Cu/Mn molar ratio 1:5.[16]

In this study, the CuMnOx nanocatalyst was synthesized and coated on 10 ppi alumina foam and used as a catalyst converter at the outlet of the vented gas space heaters.

Methods

Catalyst Preparation

The CuMnOx catalyst was prepared by the co-precipitation method. All the chemicals used were of Merck grade. A 0.25 molar solution of Mn-nitrate ($Mn(NO_3)_2.4H_2O$) was added to 0.25 molar of copper (II) nitrate ($Cu(NO_3)_2.3H_2O$) and stirred for 1 hour. Na_2CO_3 2 molar solution was added drop-wise to the nitrate solution, heated to 80°C, and stirred at 800 rpm until a pH of 8.3 was reached and a suspension was formed.[18] The resultant precipitate was stirred continuously for 2 hours at 80°C. The molar ratio of Cu/Mn in the CuMnOx catalyst was 1:2. The precipitate was then washed with hot distilled H_2O several times.[19] The spin treatment method was used to caver catalysts on alumina foam,[20] and the used alumina foam was a 10 ppi commercial ceramic foam with a diameter of 95 mm in and thickness of 20 mm. The resulting residue was dried at 105°C in static air for 16 h and calcined at 300°C for 2 h. (Figure 1)

CO Measurement

The concentration of CO was measured by an IMR 1500 gas analyzer. The IMR 1500 detects CO in the range of 1 to 1200 ppm ±1 ppm. The catalyst converter took place on the outlet of the heater, and the CO concentrations and temperatures were measured. Co concentrations were measured in different study phases. In the first step, CO was measured without any interposition and after that uncoated alumina foam was used to calculate the effect of alumina on CO conversion. Finally, the catalyst converter took place into the flue and the concentration of CO in outlet gas was measured (Figure 2).

Characterization of the Synthesized Catalyst

X-ray powder diffraction (XRD) patterns for phase identification were recorded on a Philips

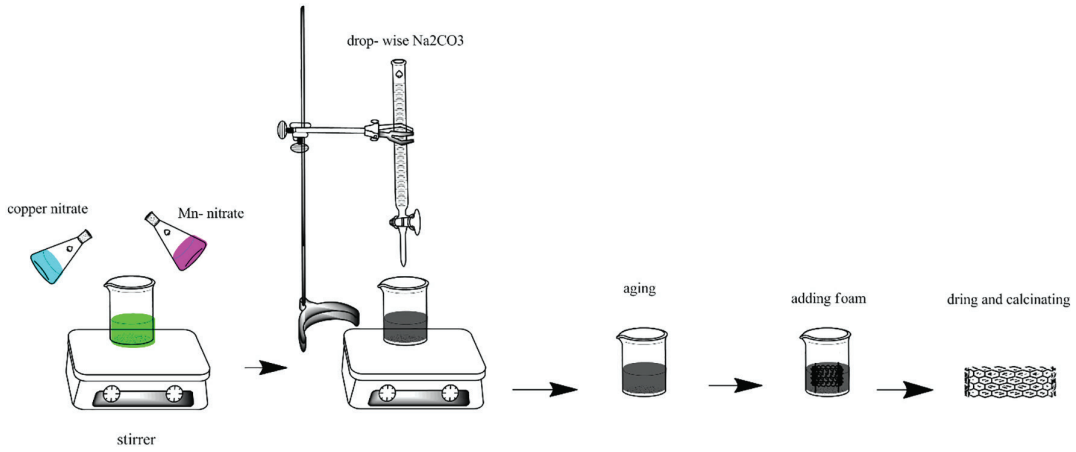

Figure 1: Graphical abstract of catalyst preparation

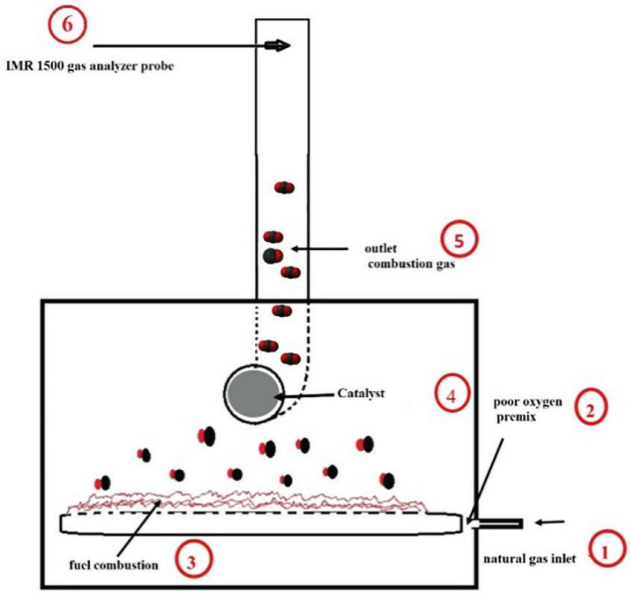

Figure 2: Graphical abstract of activity measurement.

PW1730 diffract meter, equipped with Cu LFF tube and scintillation detector. Data for cell refinements were collected in θ-2θ, the step-scan mode in the angle interval from 20 to 80, at steps of 0.05 and counting time of 1 s/step. The scanning electron microscope (SEM) image of the as-fabricated catalyst was recorded on TESCAN-Vega 3 (SEM) instrument. The accelerating voltage was used at 10 kV and magnification of the image 5000 was applied.

Results

Characterization

The textural properties of the catalysts were analyzed by scanning electron microscopy (SEM). SEM images showed granular particles in the range of 200-600 nm varying degrees of agglomeration and a layer of catalyst coated on the foam was observed (Figure 3).

Wide-angle X-ray diffraction (XRD) patterns (Figure 4) of CuMnOx were further carried out to study the crystal phases of the impregnated nanoparticles. The XRD showed quite similar diffraction peaks at around 35° and 38° for the CuMnOx sample. The average crystalline sizes can be roughly calculated by the diffraction peaks, and the average crystal size was about 30 nm. Some small peak was observed for the sample which was in the same phases with the main peak.

Catalyst Performance

The used heater was a standard model of vented gas space heaters which could be adjusted to 2300 kcal/hr and 3200 kcal/hr. In the case of 2300 kcal/hr, the highest temperature produced was about 155°C and at 3200 kcal/hr the temperature of the outlet gas was about 200°C. It took 15 minutes to reach those temperatures.

There was no significant CO removal in the case of using uncoated alumina foam and the measured

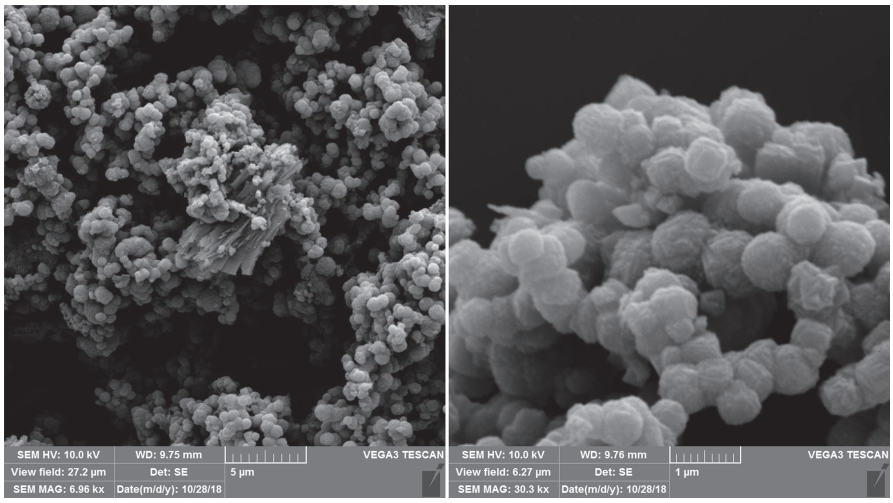

Figure 3: (a) A layer of $CuMnO_x$ was coated on alumina foam. (b), SEM image shows particle size in the range of 200 – 600 nm

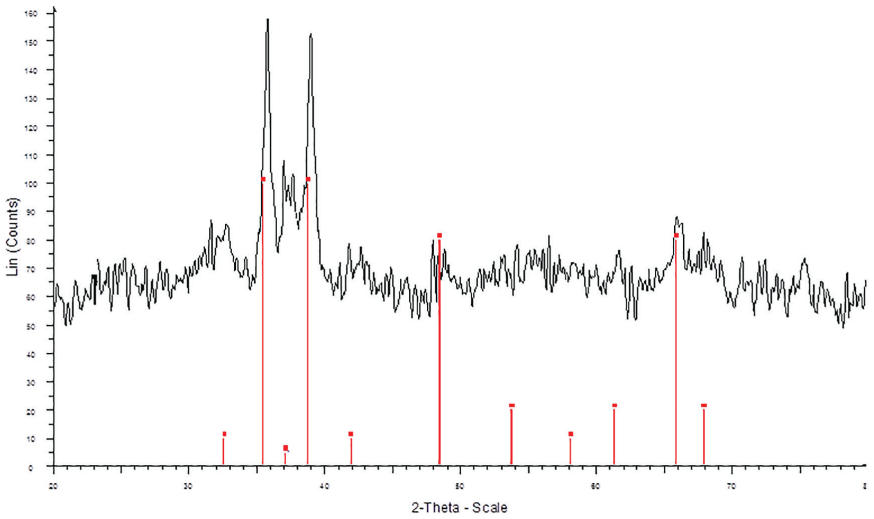

Figure 4: XRD pattern of $CuMnO_x$; the red bars show packs of crystal shape of catalyst

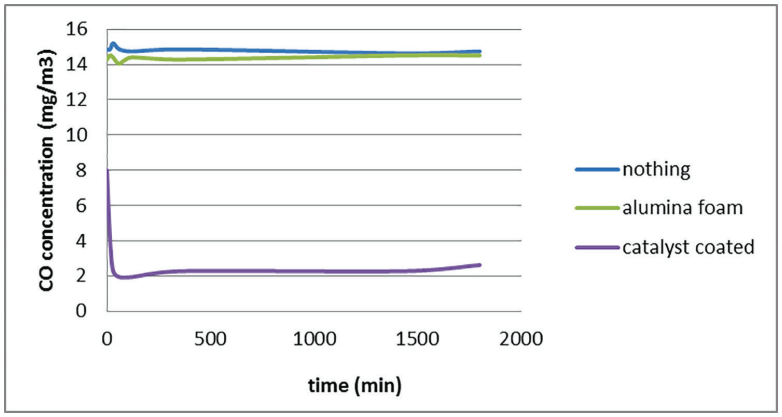

Figure 5: Using a catalyst to decrees CO from the heater in case of 2300 kcal/hr and using

CO was approximately the same as no interposition. When the foam coated with CuMnOx was placed, the CO removal was significantly increased.

Figure 5 shows the effect of using catalysts on decreasing CO concentration. As shown in this Figure, uncoated alumina foam has no considerable effect on CO removal even in the operation time of 1800 minutes. In the case of using the CuMnOx catalyst, the measured CO concentrations were decreased sharply at the beginning of the operation and remained constant until the end of the operation.

Figure 6 shows the percentage of carbon monoxide

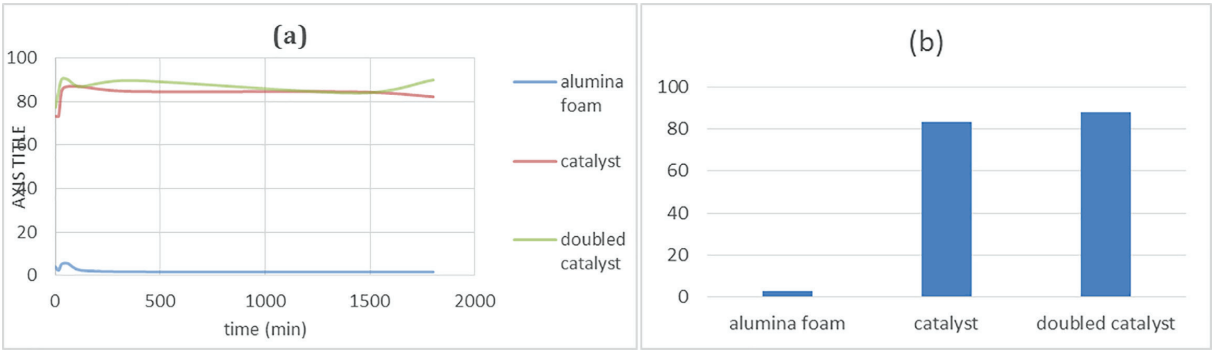

Figure 6: (a) Comparison of carbon monoxide removal efficiency during the 1800 minute, (b) comparing the average removal efficiency

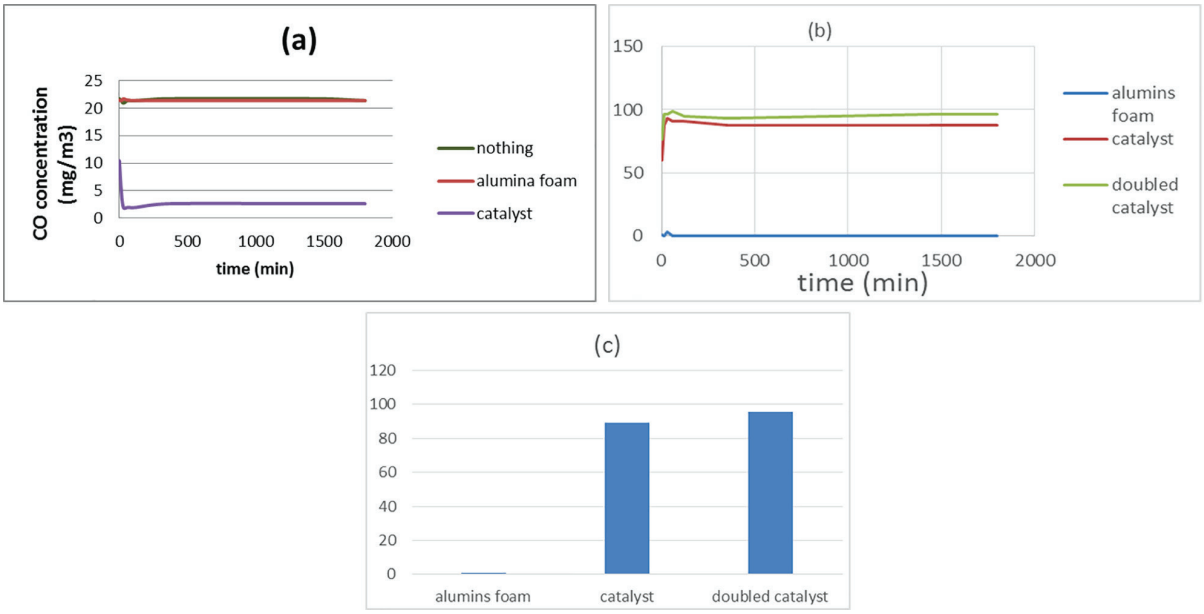

Figure 7: (a) CO emitted from the heater in 3200 kcal/h; (b) Percentage of CO removal from heater during the time; (c) average percentage of CO conversion

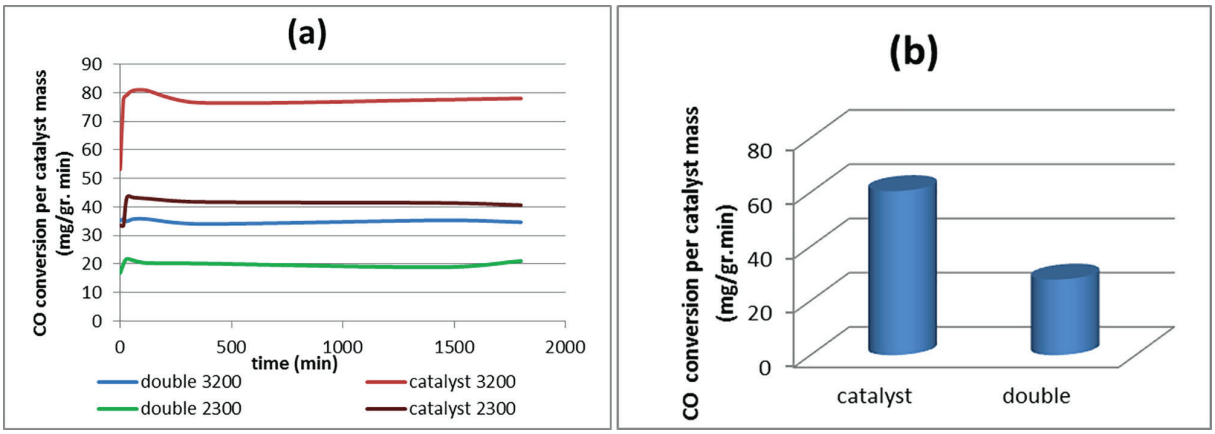

Figure 8: (a) CO conversion of catalyst in both adjustment of heater during the time; (b) average of mg CO conversion per gram catalyst per minute.

removal in heating power of 2300 kcal/hr. As the Figure shows, the use of a single catalyst leads to approximately 80% CO removal. Application of doubled catalyst (using 2 pieces of alumina foam coated with CuMnOx consecutively) has no significant effect on the CO removal in comparison with the use of a single catalyst.

Similar results were observed for the heating power of 3200 kcal/hr, as illustrated in Figure 7. The heater emitted more CO in heating power 3200 kcal/hr, but measurements showed that the removal of CO was higher than those in heating power of 2300 kcal/hr. It is due to the simultaneous increase of CO emitting and rising temperature as the temperature

plays an important role in catalyst activity.

The result of the CO conversion rate showed that the average CO converted per gram of catalyst per minuet was 60.45 mg/gr.min (129.5×10^{-3} mmol/mg.h) for the single catalyst. The corresponding value for the doubled catalyst was 27.8 mg/gr.min (59.55×10^{-3} mmol/mg.h) (Figure 8).

Discussion

It is obvious that the cold catalyst has no enough CO conversion, as shown in Figure 5. In the CO oxidation process, oxygen is first adsorbed on the CuMnOx surface with the energy of activation. When the temperature is high and adequate amount of oxygen is absorbed, any CO passing over the catalyst surfaces either reacts directly with the adsorbed oxygen or else is first adsorbed and then reacts, and after that the CO produced is desorbed.[19, 21]

Nguyen Thi studies showed 100% conversion of CO (T100) for CuMnOx catalysts at 65°C and it could be because of vapor free gas texture with 1% CO and 9 l/h flow.[22] And *Subhashish Dey* showed 50% and 100% conversion of CO for CuMnOx catalysts at 102 and 180°C, respectively.[23]

Results showed the average CO converted 129.5×10^{-3} mmol/mg.h for the single catalyst and 59.55×10^{-3} mmol/mg.h for the doubled catalyst. This is due to the doubled mass of coated catalyst and lack of a significant difference in removal efficiency. Since the major amount of CO was removed at the beginning of the catalyst and the CO concentration in the outlet is not high enough during the passage of the second piece of catalyst, the second part does not seem to have been used. *Nguyen Thi's* study showed the average 24.14×10^{-3} (mmol/mg.h) CO conversion at 35°C for CuMnOx catalyzer, which shows the importance of the role of temperature.[22]

Conclusion

Indoor sources of air pollution should eliminate as much as possible to avoid health problems. Nowadays, catalysts are among the best method to remove pollutants emitted into both indoor and outdoor environments. In this study, $CuMnO_x/Al_2O_3$ catalyst with Cu/Mn molar ratio of 1:2 was successfully prepared using the co-precipitation method and used to remove CO in the outlet gas of a vented gas space heater. As the outlet gas of heater had a high temperature, the vapor could not cause disturbance in CO conversion, so high-efficiency catalyst oxidation occurred. At the start of heater working, due to this fact that the catalyst was cold, there was no CO removal. The CO conversion occurred, while the catalyst got warm. The most important factor for catalyst oxidation was temperature. Using the proper amount of this catalyst is suggested to save people from CO poisoning in houses, offices and other microenvironments.

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Conflict of Interest: None declared.

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