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Catalytic purification of flue gas from civil-used stove

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Abstract

Effects of the method of burning and addition of catalysts in the chimney of civil-used stove on emission of air pollutants were studied. Alumina-supported copper and manganese oxides and palladium catalysts were used to purify the flue gas emitted from the civil-used stoves. The results show that, in upper burning case, both Cu–Mn–O/Al_2O_3 and Pd/CuO/Al_2O_3 catalysts can decrease the ratio of CO/CO_2 to <0.01, and remove SO_2 and volatile organic chemicals (VOC) from the flue gas to some extent. Deactivation of the catalyst results from the accumulation of sulfate groups on catalyst support. The life of the catalyst can be extended by adding a honeycomb of lime before the catalyst. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Civil-used stove; Pollutants; Flue gas purification

1. Introduction

Coal is the main fuel in China. In most small cities and downtown areas, coal is often processed into honeycomb briquettes, and people use civil-used stove to burn them for cooking and heating. However, during coal combustion, some volatile organic chemicals (VOCs), carbon monoxide and sulfur dioxide are often given off to environment [1,2,3], which cause harm to man's health, and also waste energy resources. Particularly in winter, in a room with door closed, CO and the other pollutants can accumulate in large enough quantities to endanger the health of the people and even cause death. Every winter, there have been many such accidents in China. It is estimated that the civil-used stove contributed about 30% of air pollution in urban areas in winter, and 12% of air pollution at other times. To reduce air pollution, to protect man's health and life from coal flue gas poisoning and to save energy, some new ways to purify the flue gas from civil-used stoves and promote further combustion are needed. Catalytic combustion is an effective approach for controlling the emissions of hydrocarbons, carbon monoxide, and high combustion efficiencies can be achieved at temperatures and concentrations much lower than those required for a stable homogenous gas-phase reaction to proceed [4–9]. However, combustion of powder coal often gives off a lot of suspended particles, which could accumulate on the catalyst and deactivate it. Recently, to prevent the severe air pollution caused by total suspended particulate (TSP) emitted from the powder coal combustion, the central Government of China has required manufacturers or users to innovate powder-coal boilers to shaped-coal boilers. This also provides a good opportunity to use a catalyst to clean air pollution. Hence, catalytic purification of the flue gas is becoming a very important way of controlling the air pollution caused by coal combustion. According to Refs. [4,10,11], Cu and Mn or Pd exhibit high activity for oxidation of hydrocarbons and monoxide. Alumina support is stable at high

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temperatures and, being facile, can be processed into a desirable shape.[12] Moreover, these materials are cheaper and easily obtained in China. Hence, in this work, we prepared two catalysts supported on spherical Al_2O_3 to purify the flue gas of the civil-used stove, and obtained some meaningful results.

2. Experiments

Catalysts preparation: Cu–Mn–O/Al_2O_3 was prepared by the wet impregnation method. Dried γ-Al_2O_3 (China Wenzhou Chemical Plant, BET surface area: 158.5 m^2/g, spherical shape, ∅ = 5–7 mm) was dipped in a mixed solution of $Cu(NO_3)_2$ (12 wt.%) and $Mn(NO_3)_2$(14 wt.%) for 24 h, followed by drying at 373 K for 2 h. The dried sample was then calcined at 773 K in air for 5 h. A catalyst with 8.1 wt.% of CuO and 10.2 wt.% of MnO_2 was thus obtained. To increase copper content in the catalyst, the calcined sample is again impregnated with $Cu(NO_3)_2$ solution. Copper content of the catalyst could be controlled by impregnation times.

Pd/CuO/Al_2O_3 was prepared as follows: the dried Al_2O_3 was first impregnated with a $Cu(NO_3)_2$ solution (7 wt.%, pH 5.4), dried at 373 K for 2 h, calcined at 773 K for 5 h, followed by impregnation with H_2PdCl_4 (Pd content: 9 mg/ml, pH 3.8) solution. The resultant catalyst was then dried, calcined at 723 K for 4 h, and reduced by flowing H_2 at 673 K for 2 h. A catalyst of Pd/CuO/Al_2O_3 (Pd, 0.8 wt.%; CuO, 5.4 wt.%) was obtained.

CO/CO_2 ratios were determined by GC. SO_2 in the flue gas of the chimney was measured by non-dispersive infrared spectrometer. Volatile organic chemicals (VOC) concentration in the flue gas was measured by the enriching method. GDX-101 was used as adsorbent to adsorb VOC, and the amount of the adsorbed VOC was determined by weighing the adsorbents before, and after, adsorption.

The activity of the catalyst was tested directly on a civil-used stove. Such a stove is widely used in small cities and downtown areas in China. It can hold four briquettes in the combustion chamber with a diameter of 120 mm. The primary air is directly sucked from the upper hole of the stove chamber, while the secondary air is supplied from the gate opened in the curved surface of the stove, as shown in Fig. 1. As the velocity of the secondary air can exert much influence on the emission of pollutants, in this study, the supply of secondary air is controlled at about 15 l/min.

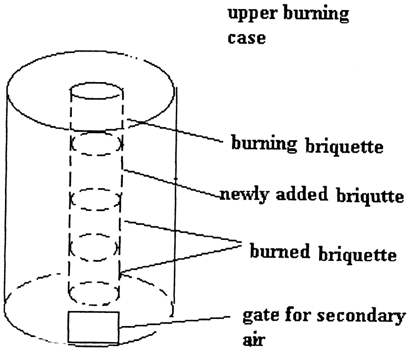

Fig. 1. Schematic picture of the stove in the upper burning case.

Each day, six honeycomb coal briquettes were combusted in the stove. The honeycomb briquette is stick-like, with a diameter of 100 mm, 110 mm high, and weighs 700 g. There are 16 channels, each with a diameter of 10 mm, evenly distributed along the stick-like briquette. The composition of the coal briquette is: C 88 wt.%, S/C 0.005. Heat output of the coal is >7000 kcal/kg. About 500 ml catalyst was placed 20 cm high above the top coal briquette and the pollutants were analyzed after they passed the catalyst bed. The mean velocity of flue gas is ca. 30 l/min.

Characterization of the catalyst: The structure of the catalysts was measured by XRD, which was carried out in Dmax-γA (Rigaku, Japan). Before measurement, the spherical sample was ground into a fine powder.

3. Results and discussions

3.1. Effect of the method of burning on the emission of pollutants

There often exist two different ways of burning while using the stove. One way is to always place the burn briquette in the upper layer of the newly added honeycomb briquette; we call it the ‘upper burning way’. Another way is to place the burning briquette at the bottom of the newly added briquette, and the new briquette is directly added to the oxidation chamber

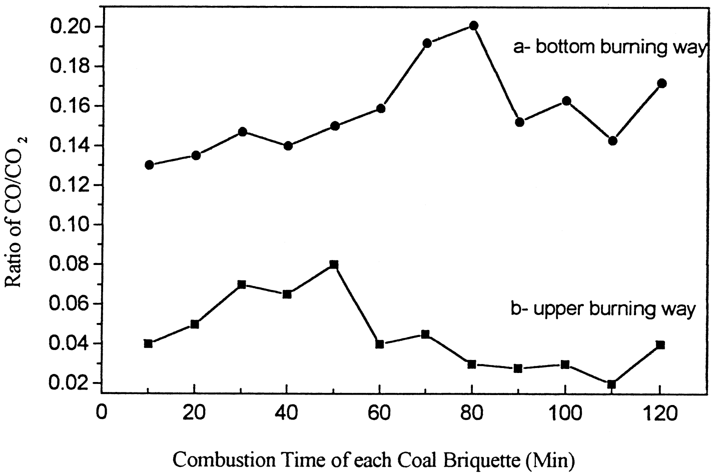

Fig. 2. Effect of method of burning on the emission of CO in the civil stove.

from the upper entrance of the stove, which is most often adopted; here, we call it the ‘bottom burning way’. Fig. 1 is the schematic diagram of a civil-used stove in the upper burning case. According to Ref. [13], the velocity of the secondary air also has much influence on the emission of the pollutants. Hence, in this study, the wind gap from the gate is kept the same in order to eliminate the effect of the secondary air.

Fig. 2 shows the changes of CO/CO_2 ratio with the combustion time of a coal briquette in different cases of burning. According to our experiments, the CO_2 concentration in the flue gas changes from 1.5 to 7.5% (in volume), and the mean concentration of CO_2 is 3.8% (in volume). It can be seen that, in the bottom burning case, the maximum value of CO/CO_2 is 0.20, and the minimum CO/CO_2 ratio is 0.13. In the upper burning case, CO/CO_2 is much lower than that in the bottom burning case. However, the maximum CO/CO_2 is 0.09, and the minimum is >0.02. The results reveal that the combustion efficiency in the upper burning case is higher than that in the bottom burning case. The reason for this lies in that, in the upper burning case, the temperature of the top briquette can always be kept at 423–573 K, when the emitted pollutants from the newly added coal briquette pass the burning briquette, they could experience a further oxidation in the high temperature zone. While in the bottom burning case, the temperature of the top coal briquette varies from 323 to 523 K, and the period at lower temperatures is quite long. The volatilized chemicals and incompletely oxidized products like SO_2 and CO are directly given off to the chimney. Thus, the emission of pollutants in upper burning case is lower than that in the bottom burning case, the upper burning way is strongly recommended. However, in Fig. 2, it is shown that CO/CO_2 is not lower than 0.01, either in the upper burning case or in the bottom burning case. According to the Japan Industrial Standards [14], only when CO/CO_2 is <0.01, the combustion can be regarded as complete. Thus, it can be concluded that our usual combustion way is not complete. In order to prevent air pollution and raise the combustion efficiency, purification of the flue gas by secondary combustion is needed.

Changes of SO_2 and VOC emission with the burning ways are shown in Fig. 4(a and b) and Table 1. It can be seen that SO_2 concentration in the flue gas changes from 135 to 60 mg/m^3 in both, the upper and bottom burning ways. The average SO_2 concentration in the flue gas in the upper burning way is lower than that in the bottom burning way, which is probably because that some of the newly yielded SO_2 from the new briquette can be adsorbed by the upper burning or burnt briquette. VOC emission in the upper burning case (0.12 mg/m^3) is lower than that in the bottom burning case (0.15 mg/m^3). The reason for this result is that, in the upper burning case, some of VOC can be

Table 1
VOC Concentration in the flue gas of the civil-used stove in different combustion cases with different catalysts

Combustion conditions	With no catalyst		Cu–Mn–O/Al_2O_3		Pd/Cu/Al_2O_3		Cu–Mn–/Al_2O_3		Pd/Cu/Al_2O_3	
	upper burning	bottom burning	upper burning	bottom burning	upper burning	bottom burning	lime upper	brick burning	lime bottom	brick burning
VOC concentration (mg/m^3)	0.12	0.15	0.09	0.10	0.07	0.08	0.07		0.06	

further oxidized and adsorbed by the burning or burnt briquette.

3.2. *Effect of addition of catalysts in the chimney of the stove on emission of pollutants*

Fig. 3 shows the variation of CO/CO_2 in the flue gas with the time of coal combustion when a catalyst is added in the chimney in the bottom burning case. When using Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2), CO/CO_2 ratio changes from 0.12 to 0.04 (Fig. 3(a)), much lower than that without a catalyst. If CuO content in the catalyst is increased to 15.3 wt.% with the MnO_2 content unchanged, CO/CO_2 becomes much lower, suggesting that increasing copper oxide in the catalyst enhances the activity of CO oxidation a great deal. However, CO/CO_2 ratio in the flue gas is still higher than the Standards Limit, showing that Cu–Mn–O/Al_2O_3 catalyst in the bottom burning case could not make the coal combust completely. When adding Pd/CuO/Al_2O_3 in the chimney, the changes of CO/CO_2 with the combustion time of each coal briquette are shown in Fig. 3(c). The CO/CO_2 ratio is lowered to 0.01, suggesting that Pd/CuO/Al_2O_3 have the highest activity for CO oxidation.

Addition of catalysts in the chimney of the stove also decreases the emission of SO_2 from flue gas, as shown in Fig. 4c and d. At the beginning of coal combustion, more SO_2 is emitted from coal combustion. This is probably owing to that the sulfur in the coal is more easily oxidized than carbon, SO_2 in the flue gas decreases from about 135 to 80 mg/m^3 after the catalyst was added in the chimney. When the generated SO_2 passes the catalyst, some of it is adsorbed or transformed into SO_4^{2-}, its concentration in the flue gas is thus reduced. Because Cu–Mn–O/Al_2O_3 and Pd/CuO/Al_2O_3 catalysts have the same support, not much difference exists between the SO_2 emissions from the two catalysts (Fig. 4(c and d)).

In the upper burning case, with the addition of Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2), VOC in the flue gas is 0.09 mg/m^3, i.e. 0.03 mg/m^3 lower than that without addition of a catalyst. On the other hand, in the bottom burning way with Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2) catalyst, VOC in the flue gas is 0.10 mg/m^3, i.e. 0.01 mg/m^3 higher than that in upper burning case. When using Pd/CuO/Al_2O_3 instead, VOC in flue gas is 0.07 mg/m^3 in the upper burning case, and 0.08 mg/m^3 in the bottom burning case. These results show that the addition of a catalyst in the chimney can decrease the emission of SO_2 to a great extent, and Pd/CuO/Al_2O_3 shows higher activity for VOC conversion than Cu–Mn–O/Al_2O_3.

3.3. *Life evaluation and the deactivation of the catalyst*

The results of life tests of different catalysts are shown in Fig. 5. It can be seen that the CO/CO_2 ratio in the bottom burning case with addition of Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2) catalyst is >0.01 when it is used for 24 days, i.e. the life of the catalyst is 24 days under such conditions. While in the upper burning case, the catalyst can be used for 34 days before the ratio of CO/CO_2 rises above 0.01. This shows that the upper burning case also holds good for extending the life of the Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2) catalyst. When adding Pd/CuO/Al_2O_3 catalyst in the upper burning case, the life of the catalyst is near 40 days. This means that Pd/CuO/Al_2O_3 has a higher catalytic activity as well as a longer life.

In order to elucidate the reasons for deactivation of the catalysts, the fresh and spent Cu–Mn–O/Al_2O_3 catalysts were characterized by XRD (Fig. 6). It

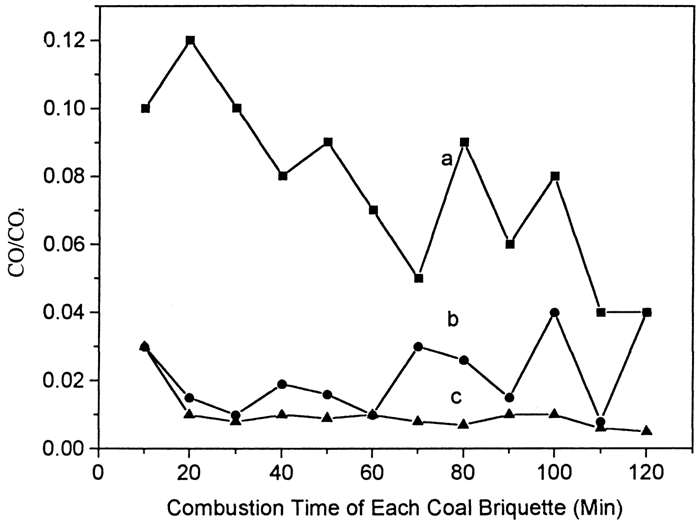

Fig. 3. Effect of addition of catalyst on the emission of CO from the civil-used stove: (a) Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2); (b) Cu–Mn–O/Al_2O_3 (15.3 wt.% CuO, 10.2 wt.% MnO_2); and (c) Pd/CuO/Al_2O_3 (0.8 wt.% Pd, 5.4 wt.% CuO).

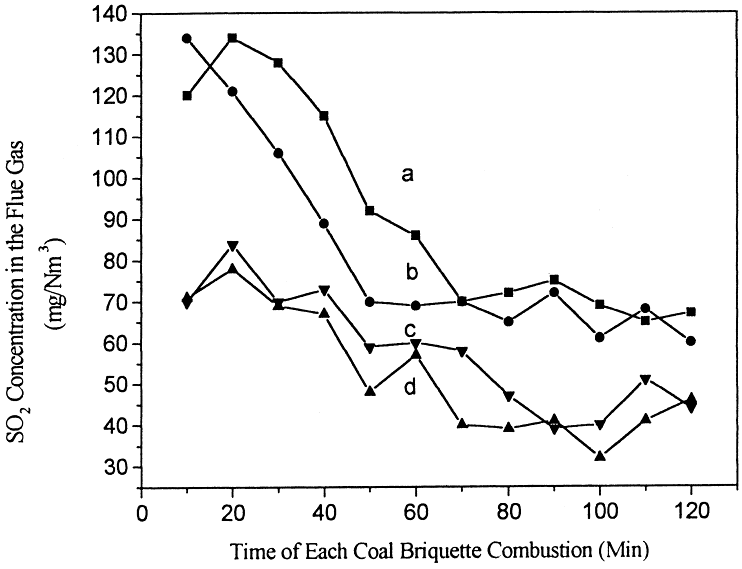

Fig. 4. Effect of combustion ways and addition of different catalysts on the emission of SO_2 from the civil-used stove: (a) bottom burning way; (b) upper burning way; (c) with Cu–Mn–O/Al_2O_3 (15.3 wt.% CuO, 10.2 wt.% MnO_2) in the bottom burning way; and (d) with Pd/CuO/Al_2O_3 in the bottom burning way.

can be seen that the active components of CuO and MnO_2 are highly dispersed in the alumina support, hence no crystalline phases are detected in the fresh catalyst by XRD. However, after the catalyst deactivates, $Al_2(SO_4)_3$, $CuSO_4$ and $MnSO_4$ are formed, which is not active for oxidation of VOC and CO. The amount of $Al_2(SO_4)_3$ increases with the life of catalyst. Hence, it can be inferred that deactivation of the catalyst results from the transformation of active components and the support to sulfates by SO_2 in the flue gas. Because the active components, such as Cu and Mn, are easy to react with SO_2 to form the

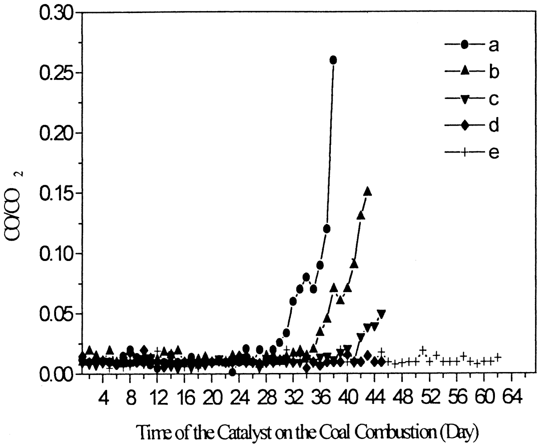

Fig. 5. Life evaluation of different catalysts in different combustion ways: (a) Cu–Mn–O/Al_2O_3 (15.3 wt.% CuO, 10.2 wt.% MnO_2) in the bottom combustion case; (b) '(a)' catalyst in the upper combustion case; (c) with Pd/CuO/Al_2O_3 (0.8 wt. Pd, 5.4 wt. CuO) in the upper burning way; (d) '(b)' with a pre-added lime briquette; and (e) '(c)' with a pre-added honeycomb lime briquette.

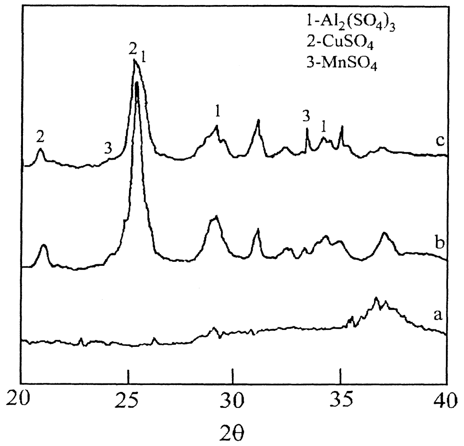

Fig. 6. XRD patterns of the spent Cu–Mn–O/Al_2O_3 catalysts: (a) fresh catalyst; (b) in the upper burning case for 1000 h; and (c) in the bottom burning way for 700 h.

inactive compounds, while Pd could be kept in the active state, even CuO and the alumina support are sulfated. The Pd/CuO/Al_2O_3 catalyst has a longer life than the Co–Mn–O/Al_2O_3 catalyst. To prolong the life of the catalyst, SO_2 in the flue gas should be decreased or removed before it passes the catalyst bed.

Fig. 5(d and e) show the life test results of the catalysts with pre-addition of lime briquettes to adsorb SO_2. It is revealed that, after running for 46 days, the activity of Cu–Mn–O/Al_2O_3 (8.1 wt.% CuO, 10.2 wt.% MnO_2) is still so high that the CO/CO_2 ratio in the flue gas could remain <0.01. For the Pd/CuO/Al_2O_3 catalyst, pre-addition of lime briquette can extend the life of the catalyst to 62 days.

Addition of lime briquette before the catalyst is also good to decrease VOC in the flue gas. If lime briquette is added before Cu–Mn–O/Al_2O_3 in the upper burning way, VOC in the flue gas can be reduced to 0.07 mg/m^3. When adopting Pd/CuO/Al_2O_3 in the bottom burning case with pre-addition of a lime briquette, VOC can be decreased to 0.06 mg/m^3.

4. Conclusions

A lot of air pollutants are generated during heating or cooking by civil-used stoves. The upper burning way is good for the further oxidation of the pollutants and to minimize the pollutants given off from the stoves.

In the upper burning case, both Cu–Mn–O/Al_2O_3 and Pd/CuO/Al_2O_3 catalysts can decrease the ratio of CO/CO_2 to <0.01, and remove SO_2 and volatile organic chemicals (VOC) from the flue gas to some extent.

Deactivation of the catalyst results from the accumulation of the sulfate group in the catalyst. The life of the catalyst can prolong by adding a honeycomb of lime before the catalyst.

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