Low Temperature Catalytic Activity of Cobalt Oxide for the Emergency Escape Mask Cartridge

Jae Man Park, Deog Ki Kim and Chang Sub Shin*

Department of Safety Engineering, Chungbuk National University, Chongju 361-763, Korea (Received October 21, 2002; Accepted November 30, 2002)

Abstract: A preparation method of cobalt supported alumina catalyst for a emergency escape mask cartridge has been studied. Catalysts were prepared by incipient wetness impregnation method using pre-shaped γ-alumina powders of 70~100 mesh. The catalyst was tested in a continuous-flow reactor system and characterized by elemental analysis, BET and TGA-DTA techniques. Cobalt shows higher activity than platinum or nickel for carbon monoxide oxidation at room temperature. Optimum loading amount of cobalt was 10 wt.% for CO oxidation and the reaction activity increases gradually with the increase of calcination temperature up to 450°C.

Key words: emergency escape mask cartridge, CO oxidation, cobalt oxide

1. Introduction

The main function of emergency escape mask is CO conversion at room temperature. Catalytic oxidation is the most effective means for carbon monoxide removement. Hopcalite(Cu-Mn mixed oxide) has been the oldest catalyst widely used for respiratory protection systems in many types of application. Improvement in activity of metal catalysts for CO oxidation has been attempted by combining manganese with other elements. Such examples are Ag/Mn and perovskike type manganite catalysts. But the catalyst for carbon monoxide oxidation has a low degree of efficiency at moderate temperature and therefore much quantity of sorbent has to be filled up.

A series of papers have been published concerning low-temperature oxidation of carbon monoxide over various transition metal oxides [1-3], but very few of these materials seem to work under realistic conditions.

Cobalt oxide catalysts have been studied several times over the years. Cobalt oxide is studied not only for its activity for carbon monoxide and hydrocarbon oxidation, but also for its use in the Fischer-Tropsch synthesis.

Yao [4] reported that cobalt oxide supported on ã-alumina had a high activity for carbon monoxide oxidation at high temperature and Jansson [5] reported the mech-

anism of low temperature carbon monoxide oxidation with a catalyst prepared by precipitation method. Also, the support influences dispersion of cobalt [6].

In this work, the effects of support, precursor and calcination on carbon monoxide conversion of cobalt catalyst are examined at low temperature to develop a cheap and effective gas mask.

2. Experimental

2-1. Preparation of Catalysts

Catalysts were prepared by incipient wetness impregnation [7] method using pre-shaped alumina μAl_2O_3 : JRC-ALO-7) powders of 70~100 mesh.

Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Merck), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Merck), platinum standard solution (H₂PtCl₆) were used as precursor compounds; aqueous precursor solutions were added to support bodies to establish a uniform loading of metal. High loadings were obtained by multiple im-pregnation with repeat of drying and calcination steps [8].

The samples were dried for overnight at 100°C and most catalyst samples were calcined in flowing air at 400°C for 2 h.

2-2. Reactor System

The catalyst was tested in a continuous-flow reactor

^{*}Corresponding author: csshin@chungbuk.ac.kr

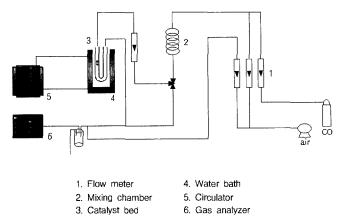


Fig. 1. Schematic diagram of experimental apparatus.

system consisting of a U-type quartz tube reactor (14 mm inner diameter) placed in a water bath, where the temperature could be controlled between 0°C and 25°C. The temperature was measured with thermocouple at the upstream of reactor (Fig. 1). A catalyst sample of 50 mg was used for the measurements and the reaction gas (0.25 vol% CO in air) was fed at the rate of 300 ml/min. The effluent gas was analyzed by gas analyzer (Quintox Co., Ltd).

2-3. Characterization

The materials were characterized by elemental analysis, BET and TGA-DTA techniques. The surface area and pore volume of the γ -Al₂O₃ were obtained by N₂-dynamic adsorption/desorption technique (p/p₀ = 0.3) using a Micromeritics ASAP2010 Instrument. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the Co/ γ -Al₂O₃ catalyst were performed on a Universal V2.5H TA Instrument.

3. Results and Discussion

3-1. Characterization

The BET surface area of the γ -Al $_2$ O $_3$ was 173 m 2 /g and total pore volume of about 0.9 ml/g and the experimentally determined TGA and DTA curves for 10 wt.% Co/ γ -Al $_2$ O $_3$ catalyst are presented in Fig. 2.

The initial weight loss of about 10% at temperature up to 110°C is attributed to the loss of water and other adsorbed species. Further weight loss of about 10% between the temperature range of 110~310°C is attributed to the nitrate decomposition of the sample. Around 400°C, the calcination was almost completed.

3-2. Effect of precursor

Fig. 3 shows the catalytic effect of metal catalysts on

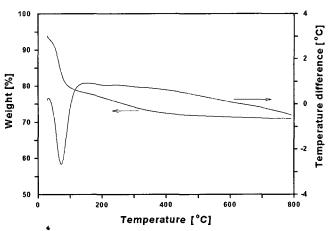


Fig. 2. Thermogram for the cobalt oxide catalyst.

oxidation reaction. The conversions of CO are over 95% in the case of cobalt oxide catalyst. On the other hand, in case of platinum and nickel oxides the conversion of CO is very low.

3-3. Influence of Loaded Amount of Cobalt on CO Oxidation Activity

Fig. 4 shows the results of CO oxidation over cobalt oxide catalysts with various Co loaded amount on γ -Al₂O₃ and calcined in 200 ml air at 400°C. The exper-

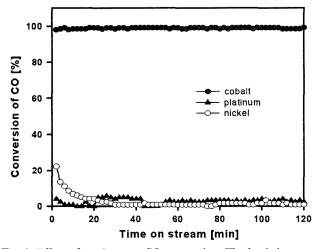


Fig. 3. Effect of catalysts on CO conversion. The loaded amount of metal was 10 wt.% Co, 1 wt.% Pt, 10 wt.% Ni and the reaction temperature was 20°C.

Table 1. Comparison of the CO conversion with different loaded amount of cobalt

Catalyst	Loading amount (wt.%)	Reaction time (min)	Conversion (%)
Cobalt/-Al ₂ O ₃	5	30	79
Cobalt/-Al ₂ O ₃	10	30	97
Cobalt/-Al ₂ O ₃	15	30	76

imental results indicated that Co loaded amount affects the activity of catalysts for CO oxidation, and the $10 \text{ wt.}\% \text{ Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst showed the highest CO conversion at 5°C for 30 min.

3-4. Influence of Calcination Temperature on CO Oxidation Activity

Fig. 5 shows the reaction results of CO oxidation over various Co/γ-Al₂O₃ catalysts calcined in 200 ml air at different temperatures of 300, 350, 400, 450 and 500°C.

Obviously, Co/γ - Al_2O_3 catalyst shows high activity for CO oxidation and the reaction activity increases gradually with the increase of calcination temperature. But above 400°C, the activity was decreased and it may be

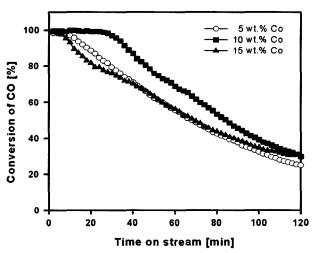


Fig. 4. Effect of loaded amount of cobalt on CO oxidation with different Co-loadings of 5, 10, 15 wt.% respectively and the re-action temperature was 5°C.

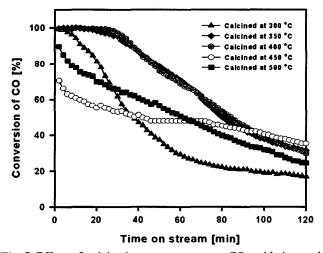


Fig. 5. Effect of calcination temperature on CO oxidation and the reaction temperature was 5°C.

Table 2. Comparison of the CO conversion with different calcination temperature

Catalyst	Calcination temperature (°C)	Reaction time (min)	Conversion (%)
Cobalt/α-Al ₂ O ₃	300	30	61
Cobalt/α-Al ₂ O ₃	350	30	95
Cobalt/α-Al ₂ O ₃	400	30	97
Cobalt/α-Al ₂ O ₃	450	30	53
Cobalt/α-Al ₂ O ₃	500	30	65

due to the aggregation of particles of Co species and the formation of large particles [9]. Table 2 shows the comparison of the CO conversion at 5°C for 30 min with different calcination temperature. The catalyst calcined at 400°C showed the highest CO conversion.

3-5. Effect of Support Material

Fig. 6 is the comparison of the effect of support on the catalytic activity. γ -Al₂O₃, TiO₂, and active carbon are used as support. Active carbon showed low efficiency at the reaction temperature of 20°C, and the cobalt supported on α -Al₂O₃ shows the highest CO conversion.

The efficiency of CO conversion was increased in the following order: $Al_2O_3 > TiO_2 > carbon$.

3-6. Efficiency of Commercial Product vs. Co/y-Al₂O₃

In Fig. 7, $\text{Co/}\gamma\text{-Al}_2\text{O}_3$ shows higher activity than commercial product. It was compared at the same reaction conditions and the amount of catalyst was 0.1 g for commercial product and 0.05 g for $\text{Co/}\gamma\text{-Al}_2\text{O}_3$. The commercial emergency escape mask provides longer than 5 minutes respiratory protection time against

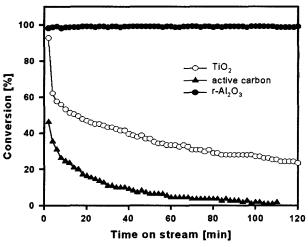


Fig. 6. Effect of support material on CO oxidation and the reaction temperature was 20°C.

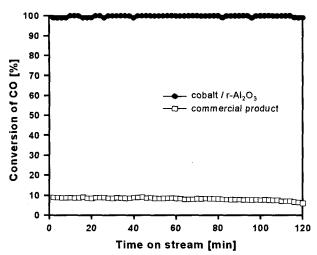


Fig. 7. Comparison of efficiency between commercial product and Co/\(\gamma Al_2O_3\) on CO oxidation and the reaction temperature was 25°C. (sample weight □: 0.1 g, ●: 0.05 g).

smoke, carbon monoxide and various toxic gases from the fire. Therefore small and effective emergency escape mask can be made by using Co/γ-Al₂O₃ catalyst.

4. Conclusion

A preparation method of cobalt supported alumina catalyst for a emergency escape mask cartridge has been proposed.

- 1) Cobalt shows the highest activity for carbon monoxide oxidation at room temperature among three metal catalysts, cobalt, platinum and nickel.
- 2) Co loading affects on the activity of catalysts for CO oxidation and it is the highest at 10 wt.%.
- 3) After calcination in air at 400°C for 2 h, the cobalt oxide catalyst exhibited the highest activity for CO oxidation and the reaction activity increases gradually with the increase of calcination temperature up to 450°C.

4) The efficiency of CO conversion was increased in the following order: γ -Al₂O > TiO₂ > carbon.

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