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Evaluation of a spinel based pigment system as a CO oxidation catalyst

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Abstract

Commercially available black pigment consisting of mixed manganese, copper and iron oxides was tested as a catalyst as well as an oxidant for CO oxidation. The crystalline structures of the catalyst were determined by XRD as $Cu_{1.5}Mn_{1.5}O_4$ mixed with Fe_2O_3 and Mn_3O_4 oxides. The fresh catalyst with 30–300 nm size and a BET surface area of 18.5 $m^2\,g^{-1}$ was able to completely convert CO at 525 °C even at a significantly high CO–O_2–He gas flow rate of 1000 ml min^{-1} (corresponding space velocity being ~310,000 h^{-1}). While the reaction rate was independent of oxygen concentration in the range tested (0.8–9.9 vol.% of O_2 at a constant CO concentration of 0.85%), it depended on CO concentration. The reaction order over fresh catalyst was measured to be 0.85 with respect to CO with an activation energy value of 47.9 kJ mol^{-1}. Application of a reduction followed by oxidation type of heat treatment on fresh catalyst induced the formation of fine clusters or domains of ~5 nm on the surface of the catalyst particles. This refined morphology with high density of defects led to a great improvement in catalytic activity. Complete CO conversion was achieved at 180 °C over a heat treated catalyst. This change in morphology also led to higher reducibility of mixed oxide system after heat treatment as indicated by TPR results. The mixed oxides of transition metals can be a viable alternative to precious metal and noble metal containing catalysts for oxidation of CO.

Keywords: Oxidation catalyst; CO oxidation; Heat treatment; $Cu_{1.5}Mn_{1.5}O_4$; Copper oxide; Iron oxide; Manganese oxide; Transition metal oxides

1. Introduction

Transition metal oxide or mixed oxides have now been established as inexpensive alternatives to precious metal and noble metal containing catalysts [1]. Noble metal catalysts are known for low temperature (near ambient or subzero) applications but they are expensive and also are prone to deactivation and poisoning. Alternatively, there are many applications of catalysts where low temperature activity is not required, for example, catalytic converters and combustion in incinerators. Thermal stability and resistance to deactivation are more important in such applications.

Copper manganese oxide mixture based on $CuMn_2O_4$ is a long established catalyst for the removal of toxic gases and vapors since its discovery in 1920 [2]. These catalysts are still the general choice for respiratory protection in mining industry to remove CO at near ambient temperatures. Moreover, it is a very effective catalyst at elevated temperatures of 200–500 °C for combustion of over 35 organic compounds and nitrogen containing compounds [3]. These mixed oxide catalysts are prepared using coprecipitation [4–10], thermal decomposition [3,11–14] and wet impregnation [15–19] methods. Fresh catalysts are subsequently calcined to optimize their activity.

It is known that many of the commercially available pigments are mixture of various transition metal oxides. In this research, we evaluated one such pigment called Black-444 from the Shepherd Color Company (CI pigment black 26) which contains manganese spinel ferrite and copper (as

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per company specified technical information). In this research, commercial pigment Black-444 (in this paper called fresh catalyst) was investigated for its potential as CO oxidation catalyst. The reaction order and activation energy was measured for the CO oxidation reaction. The effect of heat treatment on the crystalline structure and catalyst activity are discussed and compared with those of fresh catalyst. In addition, we present the results of characterization by XRD, HRTEM and TPR to elucidate the synergistic effects of mixed metal oxides.

2. Experimental

The CO oxidation ability of fresh catalyst as well as heat treated samples was measured in a horizontal flow tube setup under a continuous flow of CO gas mixture. A schematic diagram of the experimental setup is shown in Fig. 1 The catalyst bed containing ~100 mg of powder was held between two pieces of quartz wool like a sandwich at the center of 6 mm i.d. quartz tube. The quartz tube was then heated in a horizontal tube furnace (manufactured by Thermcraft Furnace) under a CO–O_2–He gas flow. While the compositions of the effluent gases were analyzed by an Infra Red (IR) detector (NGA 2000 Fisher-Rosemount MLT-4 multichannel gas analyzer) the inlet gases were controlled by Hastings digital flow meters. The temperature of the catalyst/sample was measured with a K-type thermocouple inserted into the catalyst bed. The heating rate, gas flow rate and the composition of gas mixture used varied with the type of experiments of CO oxidation and their specific values are given with specific results. A blank experiment of CO oxidation over quartz wool without any catalyst powder was performed to confirm that the wool was inert to CO oxidation reaction up to 700 °C.

In some cases, a reduction followed by oxidation type of heat treatment was applied to fresh catalysts. It involved (a) a reduction step of heating ~250 mg of catalyst spread as a thin layer on a small alumina boat at 400 °C under a 3.7%CO–He gas flow (300 cm^3/min) for 1 h; (b) cooling to ambient temperature under pure He flow; (c) an oxidation step of re-heating the sample at different temperatures (200, 320 and 500 °C) under a flow of 20% O_2–He (300 cm^3/min) for different time (1–6 h), and (d) subsequent cooling. The sample was then collected and stored in a bottle for a day before catalytic test. Heat treatment was carried out in CO oxidation setup using a larger diameter quartz tube and the furnace heating rate was fixed at 6 °C min^{-1} during the heat treatment.

The crystallographic structure of the catalyst was analyzed by X-ray diffraction (XRD) using a Philips X'Pert Pro Theta–Theta system (model PW 3040/60). Copper Kα radiation was used with operating voltage of 45 kV and tube current of 40 mA. While particle size, structure and morphology of catalysts were examined using a Philips F20 Field Emission Transmission Electron Microscope (HRTEM, Technai 200) and Topcan High Resolution Scanning Electron Microscope, surface area of the catalyst was measured by BET technique (Quantachrome Autosorb Automated Gas Sorption Unit) by absorbing helium at liquid nitrogen temperature on the catalyst surface. The elemental composition of the catalyst was analyzed using ICP-AES (for metals) and combustion analysis/Leco method (for carbon).

The reducibility of the catalyst was characterized using a Temperature Programmed Reduction technique (manufac-

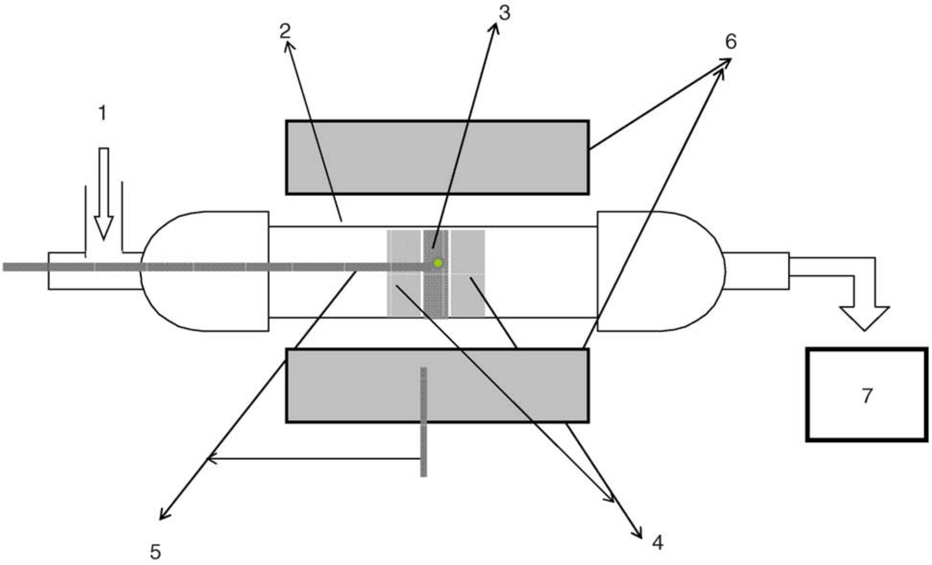

Fig. 1. Schematic diagram of CO oxidation setup: (1) gas flow inlet, (2) quartz tube, (3) catalyst bed, (4) quartz wool, (5) K-type thermocouple, (6) tube furnace, (7) multi-channel gas analyzer.