

PA23) On-stream Performances in Catalytic  
Oxidation of CO over  $\text{CoO}_x/\text{TiO}_2$  at Low  
Temperatures

Ki-Hwan Kim, Moon-Hyeon Kim\*<sup>1)</sup>

Department of Environmental Engineering Daegu University

### 1. Introduction

Homogeneous charge compression ignition (HCCI) combustion has been proposed to be an alternative and attractive technology for internal combustion engines that can offer a great potential of high thermal efficiencies, comparable to or greater than conventional diesel engine vehicles, and dramatic reduction in  $\text{NO}_x$  and particulate matter (PM) emissions [1,2]; therefore, HCCI engine-equipped automobiles are probably one of the most promising candidates to meet very stringent future emission standards. One of the current challenges to the HCCI technology for road applications is to control CO and unburned hydrocarbons (HCs) emissions with concentrations greater than 1%.

A huge body of candidates have been proposed for low-temperature CO oxidation to date and there exist very promising catalysts for the HCCI applications, depending on their preparation techniques, activation protocols and testing conditions. Supported or promoted CuO systems have been studied as substitute catalysts for low-temperature CO oxidation [3-12], and CuO-CeO<sub>2</sub> mixed oxides are highly active and exceptionally selective for the oxidation reaction. Recently, Pillai and Deevi [13] have reported un-promoted and unsupported CuO that was obtained via a precipitation method following an activation process in flowing O<sub>2</sub>/CO, and this catalyst gives complete CO oxidation even at ambient temperature.

Unsupported and supported cobalt oxides have been well known to be quite active for CO oxidation at very low temperatures [11,12,14-18]. Unsupported Co<sub>3</sub>O<sub>4</sub> powders possess high, reproducible activity for catalytic CO oxidation at temperatures greater than 150°C, depending significantly on calcination temperatures used, although the rate of the CO conversion could decrease in the presence of HCs, NO, and H<sub>2</sub>O [14]. A similar observation is reported by Teng et al. [17] who yielded 100% CO conversion at 150°C with unsupported Co<sub>3</sub>O<sub>4</sub> even in the presence of excess H<sub>2</sub>. However, much higher performance, based on temperatures exhibiting 100% CO conversion, is indicated for a pure

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\* Corresponding author.

Co<sub>3</sub>O<sub>4</sub> catalyst, obtained via the calcination of precipitated cobalt carbonates at 400°C, on which complete CO conversion around -50°C occurs when a CO-O<sub>2</sub> reaction mixture was specially dehumidified [18]. Cobalt oxides dispersed on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and SrCO<sub>3</sub> have been frequently used for the oxidation of CO at low temperatures [16,19-24], and it is shown that the extent of catalytic CO conversion in the oxidation reaction depends on the supports and pretreatment procedures used. This study reports significant differences in CO oxidation activity at low temperatures between TiO<sub>2</sub>-supported CoO<sub>x</sub> catalysts calcined consecutively at a given temperature.

## 2. Experimental

Pure powder-type TiO<sub>2</sub> (Millennium Chemicals, DT51D, S.A. = 87 m<sup>2</sup>/g) was used to prepare a supported CoO<sub>x</sub> catalyst. Prior to dispersing the CoO<sub>x</sub> onto the TiO<sub>2</sub>, it was calcined at 570°C for 4 h in flowing air (Praxair, 99.999%) at 1000 cm<sup>3</sup>/min. CoO<sub>x</sub>/TiO<sub>2</sub> catalyst containing 5 wt% CoO<sub>x</sub> based on the Co element was obtained by incipient wetness in which an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 99.999%) was impregnated dropwise, as described elsewhere [25,26]. After the simple impregnation, this catalyst was dried in air overnight at 110°C.

Each activity profile for CO oxidation at either 50 or 100°C over 5 wt% CoO<sub>x</sub>/TiO<sub>2</sub> samples after calcination at different temperatures was obtained using a continuous flow fixed-bed type U-shaped Pyrex reactor placed in a bottom-capped cylindrical electric furnace. A sample of either 0.33 or 0.65 g catalyst was placed above a quartz wool plug in the Pyrex reactor and routinely calcined at 350, 450 or 570°C for 1 h in situ in flowing air at 100 cm<sup>3</sup>/min using a Brooks 5850E mass flow controller, prior to being used for the catalytic oxidation of CO (AGT, 99.998%). The air was purified by flowing it through an Alltech moisture trap.

A typical gas mixture consisting of 1% CO and 3% O<sub>2</sub> in flowing He (Praxair, 99.999%) at a total flow rate of either 100 or 200 cm<sup>3</sup>/min, corresponding to a gas hourly space velocity (GHSV) of 6,000 - 24,000 h<sup>-1</sup>, was passed over the catalyst bed for CO oxidation at temperatures ranging from 50 to 100°C. All the gas flow rates during on-stream activity measurements were controlled using Brooks 5850E and MKS Type 1179A mass flow controllers. The effluent gases were analyzed using an on-line, computer-controlled Shimadzu 2014 gas chromatograph equipped with a thermal conductivity detector and a CTR I concentric column (Alltech Assoc.) for CO<sub>2</sub>, CO and O<sub>2</sub> separations in single analysis.

## 3. Results and Discussion

An activity profile of the 5 wt% CoO<sub>x</sub>/TiO<sub>2</sub> catalyst calcined at 350°C for CO oxida-

tion at 50°C are shown in Fig. 1. The supported  $\text{CoO}_x$  catalyst after calcination at 350°C had a 100% CO conversion when measured after  $\sim 1$  h on stream; this conversion was stable for 20 h. The on-stream activity decreased gradually with reaction time, and after 450 h catalytic performances near 5% were observed with this sample. This was in good agreement with earlier results with unsupported  $\text{Co}_3\text{O}_4$  powders which represented a gradual decrease in activity with time for CO oxidation at ambient temperature [11,18,20]. All CO conversions were consistent with  $\text{CO}_2$  production rates during the oxidation reaction.

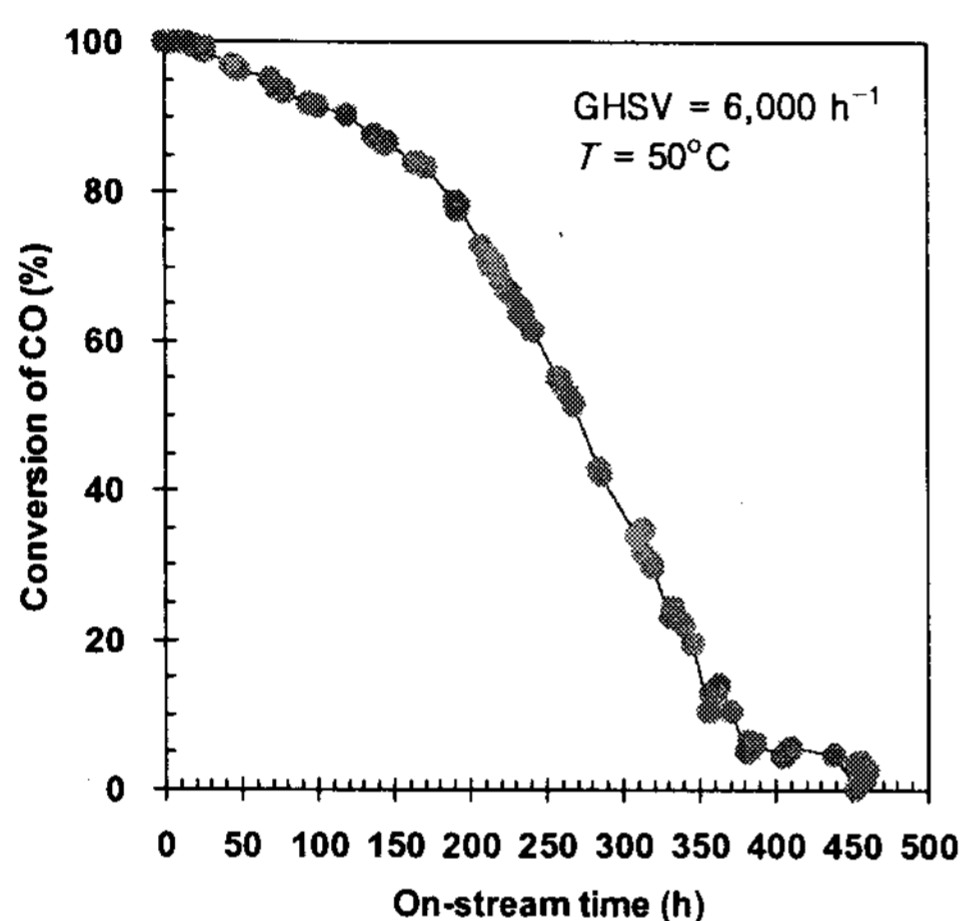


Fig. 1. On-stream activity for CO oxidation over 5 wt%  $\text{CoO}_x/\text{TiO}_2$  after calcination at 350°C.

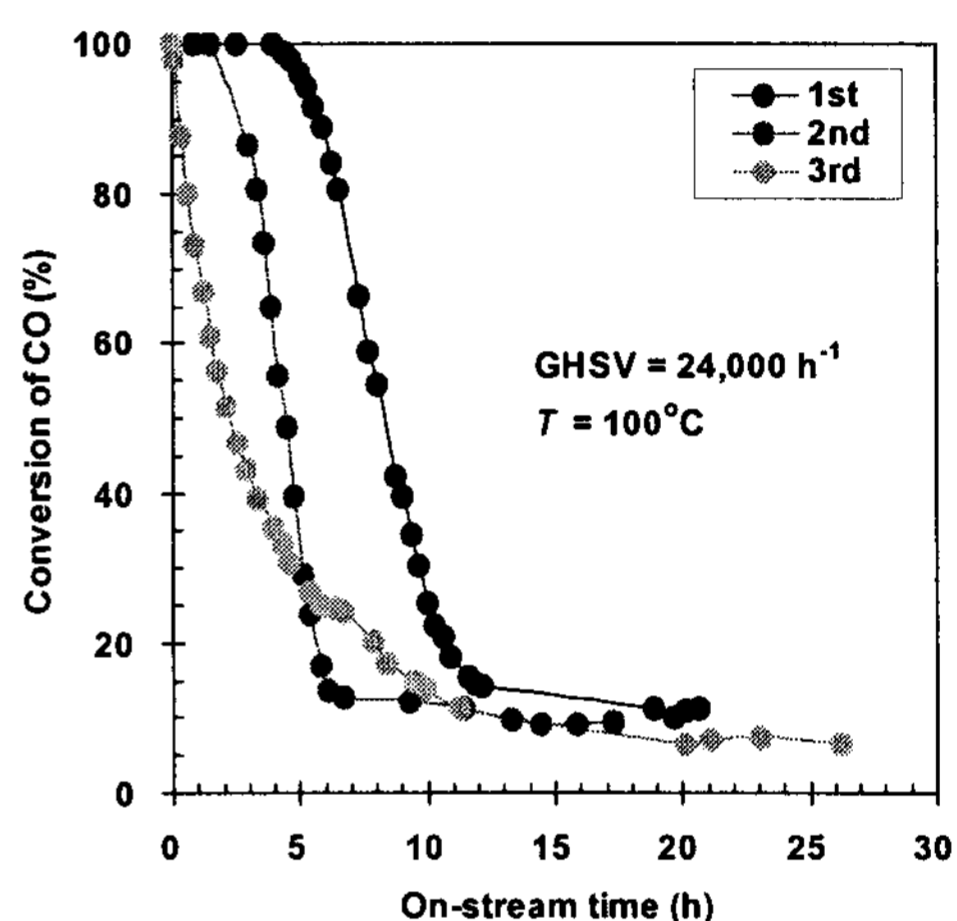


Fig. 2. Effect of calcination excursion at 350°C on 5 wt%  $\text{CoO}_x/\text{TiO}_2$  for CO oxidation at 100°C.

To provide a direct measurement of the effect of calcination excursion on 5 wt%  $\text{CoO}_x/\text{TiO}_2$ , a single sample of this catalyst was first calcined at 350°C in situ in the reactor before CO oxidation at 100°C, and then the sample was subjected to 2 times consecutive calcinations at the same temperature following the respective CO oxidation. 100% CO conversion was achieved after the first 350°C calcination and maintained for about 4.5 h from which the catalytic activity became decrease with on-stream hours, as demonstrated in Fig. 2. If this sample was again calcined at the temperature, the on-stream hours exhibiting 100% activity was shorter. Thus it is clear that the activity of this  $\text{TiO}_2$ -supported  $\text{CoO}_x$  catalyst for CO oxidation at 100°C depended strongly on thermal excursion for calcination.

#### 4. Conclusions

A 5 wt%  $\text{CoO}_x/\text{TiO}_2$  catalyst is highly active for the oxidation of CO at low temper-

atures, such as 50 and 100°C, under a purely oxidizing condition, but the extent of CO conversion is strongly dependent on thermal excursion for calcining this catalyst at 350°C. This is probably associated with the formation of carbonates on the surface of the catalyst or surface reconstruction.

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