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Low-temperature Oxidation of CO over CoOx/TiO₂ Catalysts for HCCI Applications

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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 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, e.g., Tier 2 program in the United States and EURO 5 in Europe. 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%.

Unsupported and supported cobalt oxide catalysts have been well known to be quite active for CO oxidation at very low temperatures [3-6]. Unsupported Co_3O_4 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_2O [3]. A similar observation is reported by Teng et al. [4] who yielded 100% CO conversion at 150°C with unsupported Co_3O_4 even in the presence of excess H_2. However, much higher performance, based on temperatures exhibiting 100% CO conversion, is indicated for a pure Co_3O_4 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_2 reaction mixture was specially dehumidified [6]. Cobalt oxides dispersed on Al_2O_3, SiO_2, MgO, La2O3, CeO_2, and $SrCO_3$ have been frequently used for the oxidation of CO at low temperatures [5,7-10], and it is shown that the extent of catalytic CO conversion in the oxidation reaction depends on the supports and pretreatment procedures used.

Although low-temperature CO oxidation reactions under net oxidizing conditions have been examined on the supported CoO_x catalysts [5,7-10], we could find, to the best of our knowledge, no studies of TiO_2-supported CoO_x catalysts for CO oxidation at low temperatures, except for only an earlier work of Epling et al. [11] whose results indicated that a CoO_x/TiO_2 catalyst after calcination at 500°C can be as active for CO oxi-

dation at temperatures ranging from 130 to 180°C as TiO_2-supported Pt-based catalysts. This study reports significant difference in activity between TiO_2-supported CoO_x catalysts after calcination at different temperatures for CO oxidation at low temperatures.

2. Experimental

A powdered TiO_2, commercially referred to as DT51D, was received from Millennium Chemicals, and this TiO_2 employed to prepare a supported CoO_x catalyst consists of pure anatase structure and has a specific surface area of 87 m^2/g. Prior to loading the CoO_x onto the TiO_2, it was calcined at 570°C for 4 h in flowing air (Praxair, 99.999%) at 1,000 cm^3/min. CoO_x/TiO_2 catalyst containing 5 wt% CoO_x based on the Co element was obtained by an incipient wetness technique in which an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.999%) was impregnated dropwise [12]. After the impregnation, this catalyst was dried in air overnight at 110°C and stored in a desiccator for later use.

Each activity profile for CO oxidation at 100°C over 5 wt% CoO_x/TiO_2 samples after calcination at different temperatures was obtained using a continuous flow fixed-bed type U-shaped Pyrex reactor with catalyst bed placed in a bottom-capped cylindrical electric furnace coupled with a PID temperature controller (Hanyoung NP200). Typically 0.4 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 cm3/min using a Brooks 5850E mass flow controller, prior to being used for the catalytic oxidation of CO (Matheson, 99.99%). The air was purified by flowing it through an Alltech moisture trap. A typical gas mixture consisting of 1% CO and 3% O_2 in flowing He (Praxair, 99.999%) at a total flow rate of 100 cm3/min, corresponding to a gas hourly space velocity (GHSV) of 12,000 h-1, was passed over the catalyst bed for CO oxidation at 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 Agilent 6890N gas chromatograph equipped with a thermal conductivity detector and a Porapak Q column and a molecular sieve 13X column (Alltech Asso.) for the respective CO_2 and CO separations, and the CO_2 concentration produced was used for verifying the mass balance.

3. Results

Activity maintenance profiles of the 5 wt% CoO_x/TiO_2 catalyst calcined at 350, 450 and 570°C for CO oxidation at 100°C are shown in Fig. 1 with that for the bare TiO_2. The supported CoO_x catalyst after calcination at 350°C had a 38-% conversion for the oxidation when measured at an on-stream time of 4 min, and this conversion was maintained unchanged for 2 h on time. The calcination of the catalyst at 450°C gave CO con-

versions near 82% for all continuous operating hours covered here, which was much higher than that indicated after calcination at 350°C. Surprisingly, CO conversions below 2% were observed for all on-stream hours allowed, when the catalyst was calcined at 570°C. The bare TiO₂ used as the support was shown to be completely inactive for this low-temperature CO oxidation reaction, in good agreement with earlier results [11,13]. All the measured CO conversions were very consistent with that based on the concentration of CO_2 produced during the oxidation reaction. In an independent measurement of the activity for CO oxidation with 5 wt% CoO_x/TiO_2 after calcination at 450°C, this catalyst had stable conversions around 80% even for 18 h on stream (not shown).

Figure 2 shows in situ TPD spectra for 5 wt% CoO_x/TiO_2 after calcination at either 450 or 570°C following exposure to 1% CO in flowing He at 50°C. The sample calcined at 450°C possessed an intense CO desorption peak at 143°C along with a weak shoulder at 216°C, as displayed in Fig. 2a. This main desorption peak position had a higher temperature, by 80°C, than that reported by Thormahlen and co-workers [5], but their CoO_x/Al_2O_3 catalyst was calcined at 550°C for 1 h and subsequently reduced at 627°C for 10 min. The spectrum for CO desorbed from the catalyst, which had been calcined at 570°C, gave a very weak peak at 87°C (Fig. 2b). In either case, no CO desorption peaks appeared at temperatures above 250°C.
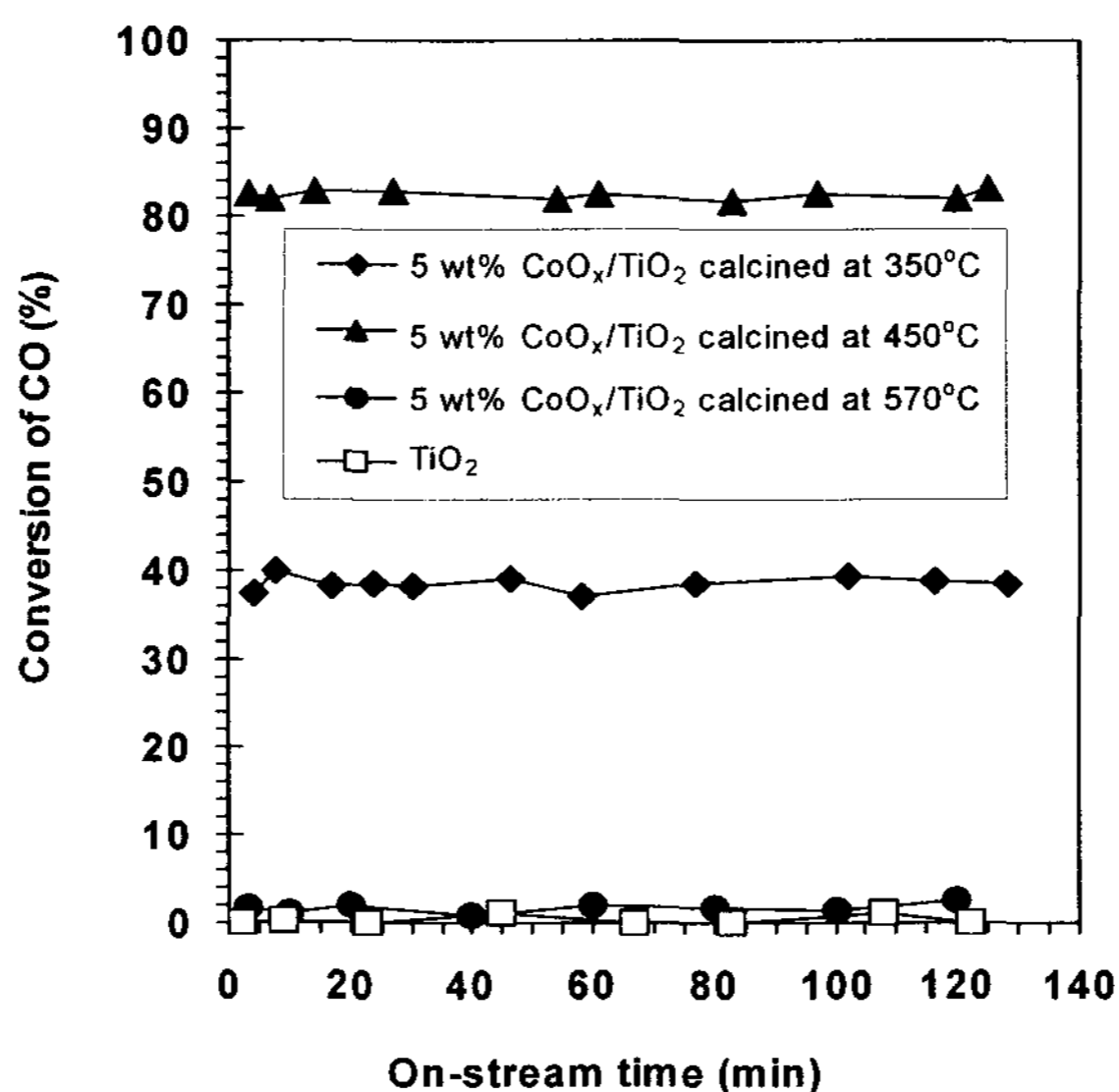

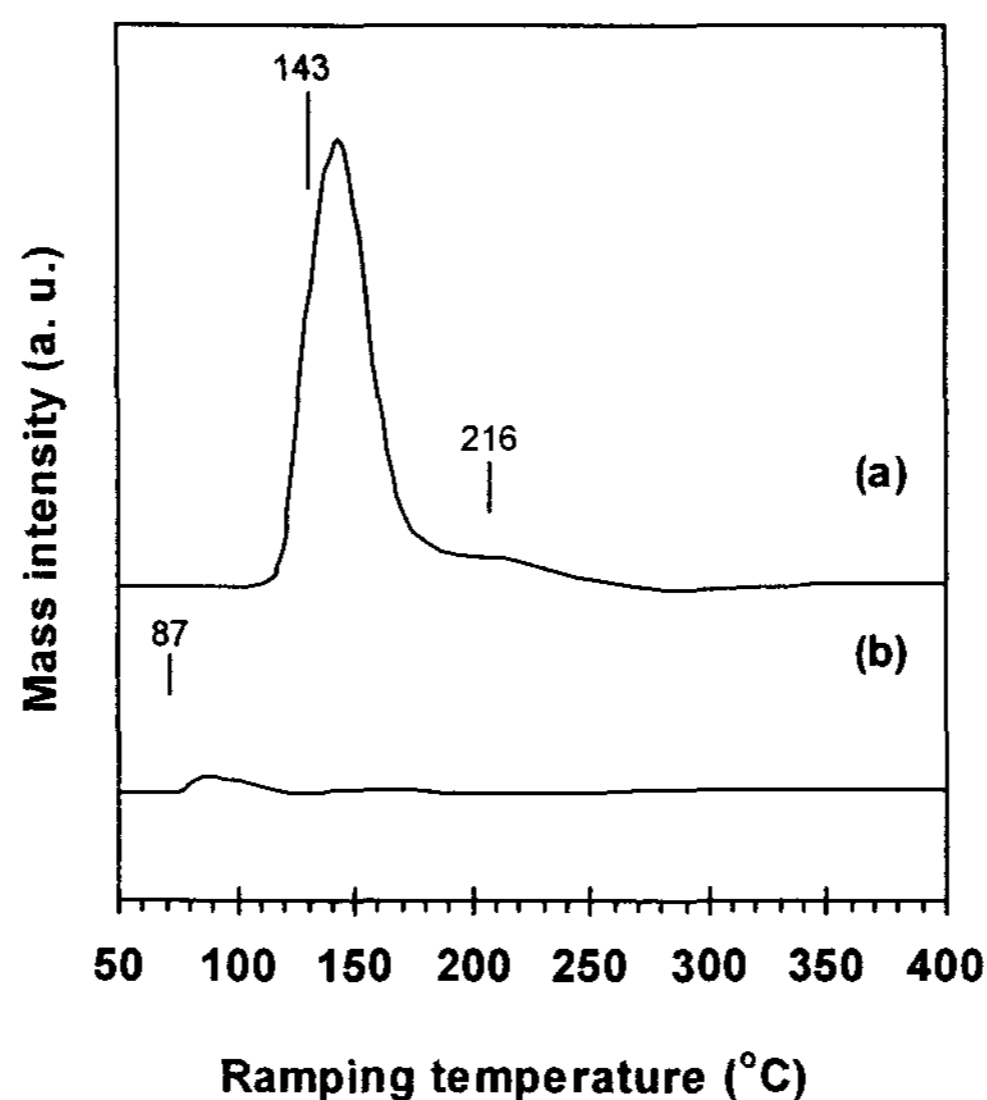Fig. 1. Catalytic activity for CO oxidation at 100°C over 5 wt% CoOx/TiO₂ after calcination at different temperatures.

Fig. 2. TPD spectra for CO adsorbed at 50℃ on 5 wt% CoOx/TiO₂ after calcination at: (a) 450; (b) 570℃.

4. Discussion

The time-on-stream activity of 5 wt% CoO_x/TiO₂ for the catalytic oxidation of CO at 100°C under a purely oxidizing condition depends dramatically on temperatures to calcine this catalyst, and the range of indicated CO conversions is practically zero to 82%, as given in Fig. 1. Although unsupported Co_3O_4 powders for CO oxidation at ambient temperature had a gradual decrease in activity with time [6,8], the supported CoO_x catalyst exhibits no deactivation for 2 h at least, irrespective of calcination temperature used here. Among CoO_x/TiO₂ samples calcined at different temperatures, the catalyst calcined at 450°C has highest activity for CO oxidation reaction at 100°C and is much more active than earlier reported Co/Al₂O₃ catalysts that were calcined at 500°C for 2 h and subsequently reduced at temperatures ranging from 350 to 450°C in a flow of pure H₂ [7,10]. However, almost zero activity is observed with the catalyst following calcination at 570°C for all operating hours. If a sample of 5 wt% CoO_x/TiO₂ calcined first at 450°C is brought to the calcination at 570°C, it has very low CO conversions near zero (Fig. 2), suggesting that active surface CoO_x species existing with the catalyst after calcination at 450°C may be irreversibly altered to an inert Co phase upon the higher temperature calcination. Negligible CO chemisorption on such Co species inactive for CO oxidation reaction occurs, as observed by in situ TPD spectra in Fig. 2. Cobalt-based catalysts dispersed on porous solid materials, such as SiO₂, Al₂O₃, and TiO₂, are widely used for industrial Fischer-Tropsch synthesis processes, and relatively high-temperature calcination of these supported cobalt catalysts could produce different Co species, e.g., Co_2SiO_4,

$CoAl_2O_4$, $CoAlO_4$, and $CoTiO_3$, by a change in the metal-support interface due to the strong metal-support interaction (SMSI), except for Co_3O_4 and CoO formation [14-17]. Consequently, the dramatic effect of the calcination temperature on the activity in this low-temperature CO oxidation over 5 wt% CoO_x/TiO_2 is associated with the formation of inactive Co-containing species on the support by the SMSI effect.

5. Conclusions

A 5 wt% CoO_x/TiO_2 catalyst is highly active for the oxidation of CO at low temperatures, such as $100^{\circ}C$, under an oxidizing condition, but the extent of CO conversion depends strongly on calcination temperatures of this catalyst. The most promising performance was obtained with the catalyst after calcination at $450^{\circ}C$ to form Co3O4 nanoparticles highly active for this oxidation reaction. Practically zero activity was revealed with a sample of the catalyst, that had been subjected to calcination at $570^{\circ}C$, for all on-stream hours tested, and this is probably due to the formation of cobalt titanates.

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