

Durability of Supported CoO_x Nanoparticles for Low-Temperature CO Oxidation

Ki-Hwan Kim^{*}, Moon Hyeon Kim^{*,†} and Sung-Won Ham^{**}

^{*}Department of Environmental Engineering, Daegu University
15 Naeri, Jillyang, Gyeongsan, Gyeongsan 712-714, Korea, moonkim@daegu.ac.kr

[†]Corresponding author

^{**}Department of Display and Chemical Engineering, Kyungil University
33 Buho, Hayang, Gyeongsan, Gyeongsan 712-714, Korea, swham@kiu.ac.kr

ABSTRACT

On-stream durability of TiO₂-supported CoO_x catalysts, which had been prepared via incipient wetness technique, in the oxidation of CO has been inquired as a function of reaction parameters, such as CoO_x contents, O₂ and CO concentrations and reaction temperatures, and samples deactivated under such different conditions have been characterized using XRD, XPS, Raman and BET area measurements, and the analysis of elemental carbon deposited on the surface. The stability of CoO_x/TiO₂ during the course of CO oxidation reaction at 100°C had primarily a strong dependence on CoO_x loadings; a sample of a 5 wt% CoO_x/TiO₂ catalyst gave a 100-% CO conversion up to 5 h after which the activity decreased with time and reached to conversions near 10%, while very rapid deactivation with 1 wt% CoO_x occurred with 10 min. Repeated calcinations and measurements on a single sample of the 5 wt% CoO_x catalyst altered the duration in the oxidation reaction. Other variables also caused distinctive behavior in the oxidation reaction. Characterization of the 5 wt% CoO_x catalysts subjected to different reaction conditions suggests that surface reconstruction and carbonaceous materials deposition all may be associated with such duration impairment.

Keywords: CO oxidation, cobalt oxide nanoparticles, duration, deactivation, carbonaceous species

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 (NO + NO₂) 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 emissions with concentrations

greater than 1%. Supported cobalt oxides (CoO_x) are shown to be highly active for CO oxidation reaction even at temperatures lower than 150°C [3,4].

We have recently studied CO oxidation at 100°C over CoO_x/TiO₂ catalysts that were prepared using TiO₂ pellets with binders and exhibited the highest steady-state activity when calcined at 450°C [5]. However, much longer activity maintenance has been indicated for a 5 wt% CoO_x catalyst, dispersed on pure TiO₂, after calcination at 350°C [6]. We are of particular interest to the durability of this CoO_x/TiO₂ system in the oxidation as a function of a variety of reaction parameters.

2 EXPERIMENTAL

CoO_x catalysts supported on pure TiO₂ (Millennium Chemicals, DT51D, S.A. = 87 m²/g) and having different CoO_x contents were prepared by incipient wetness as described earlier [5,6]. Prior to dispersing the CoO_x onto the TiO₂, it was powdered and calcined at 570°C for 4 h in flowing air (Praxair, 99.999%) at 1000 cm³/min. After the simple impregnation, this catalyst was dried in air overnight at 110°C and stored in a desiccator for later use. The physicochemical properties of the prepared catalysts are listed in Table 1.

Catalyst	Co amount (wt%)	S _{BET} (m ² /g)	Crystallite size ^a (nm)
Pure TiO ₂	-	87	-
CoO _x /TiO ₂	1	-	-
	5	79	11
	8	-	-
	12	-	-

^a Based on Co₃O₄ acquired by XRD measurements.

Table 1: Physicochemical properties of CoO_x/TiO₂ catalysts used for CO oxidation at 100°C.

On-stream durability of the catalysts in the oxidation of CO (AGT, 99.998%) at 100°C was measured using a continuous flow type fixed-bed U-shaped Pyrex reactor. A typical gas mixture consisting of 1% CO and 3% O₂ (unless stated) in flowing He (Praxair, 99.999%) at a total flow rate of 200 cm³/min using a Brooks 5850E mass flow controller, corresponding to a gas hourly space velocity (GHSV) of

24,000 h⁻¹, was employed for the oxidation reaction. Unless otherwise specified, all the samples were calcined at 350°C before reaction and the GHSV value was employed. All the gases used here were purified by flowing them through an Alltech moisture trap and Oxytrap.

Change in CO concentration during the oxidation, thereby forming CO₂ as a product, was measured using a Shimadzu 2014 gas chromatograph equipped with a TCD detector and a CTR I column (Alltech Assoc.) to estimate on-stream performances of each sample.

Crystallite phases of supported CoO_x catalysts used for the oxidation were determined by X-ray diffraction (XRD) measurements. Pure Co₃O₄ (Aldrich, 99.995%) was employed as a reference. XRD spectra of all samples were collected *ex situ* using a Rigaku D/MAX2500 PC diffractometer equipped with a Cu Kα, (λ = 1.54056 Å) radiation source and a graphite monochromator. The respective X-ray tube voltage and current during the data collection were 40 kV and 20 mA. Each sample was loaded onto a thin quartz holder with a 12-mm diameter in the diffractometer and scanned from a 2θ value of 10 to 80° at a normal scanning rate of 2.0 °/min. Subsequently, a high resolution scanning rate of 0.1 °/min was allowed to obtain more accurate peaks of Co₃O₄ in the used samples, and average crystallite sizes for the Co₃O₄ were determined based on linewidth at half height of the XRD peak at 2θ = 31.26° by the crystallographic (220) plane using the Scherrer equation with Warren's correction for instrumental line broadening.

A VG Scientific ESCALAB 220-IXL X-ray photoelectron spectrometer, giving a dynamic vacuum below 10⁻¹⁰ Torr (1 Torr = 133.3 Pa), with an unmonochromatized Mg Kα photon source having a radiation energy of 1253.6 eV, was used to obtain Co 2p, O 1s, Ti 2p X-ray photoelectron spectroscopic (XPS) spectra for 5 wt% CoO_x/TiO₂ calcined at 350-570°C as well as deactivated under different reaction conditions. These XPS spectra were compared to those obtained with Co₃O₄ and Co_nTiO_{n+2} (CoTiO₃ and Co₂TiO₄) to determine surface chemical oxidation states of Co species. An appropriate amount (ca. 10 mg) of each sample was loaded into a pelletizer with a 10-mm diameter and pressed to obtain a thin self-supporting wafer, as described earlier [5]. All XPS spectra for the samples were recorded with a scan number of 10-15 and corrected using the C 1s peak at 284.8 eV. In addition, samples of the catalyst deactivated for the oxidation reaction was characterized via a triple Raman spectroscopy (Horiba Jobin Yvon, Model T64000) and carbon analysis.

3 RESULTS AND DISCUSSION

The extent of activity maintenance, as a basis of total conversion, on catalysts with CoO_x amounts smaller and greater than 5 wt%, at which 100% CO conversion had maintained for 5 h [6], was of particular interest to us because of the need to ascertain their effect on the duration

in the oxidation reaction. A 85-% initial activity was obtained for a 1 wt% CoO_x catalyst, and it decreased rapidly with time and became zero since 7 h, as shown in Fig. 1.

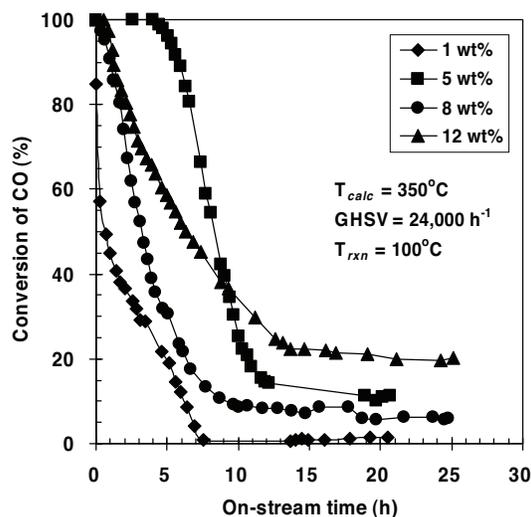


Figure 1: Activity profiles for CO oxidation at 100°C over CoO_x/TiO₂ calcined at 350°C as a function of CoO_x loading.

Samples with 8 and 12 wt% CoO_x also gave a short residence in a period of total oxidation, although the both catalysts possessed higher steady-state conversion, depending on the CoO_x contents. It is clear that the durability of this supported catalyst in the oxidation reaction was determined by its CoO_x content. Surprisingly, repeated calcinations at 350°C and measurements on a single sample with 5 wt% CoO_x altered the duration in the oxidation reaction, as provided in Fig. 2.

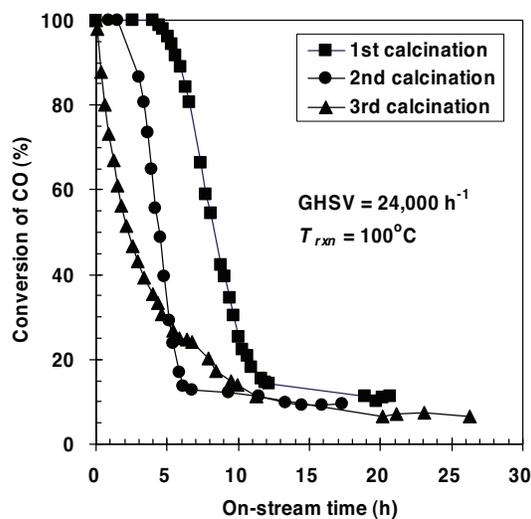


Figure 2: Duration for CO oxidation at 100°C with a single sample of 5 wt% CoO_x/TiO₂ after repeated calcinations at 350°C.

5 wt% $\text{CoO}_x/\text{TiO}_2$ catalysts after only a single calcination at 350°C following CO oxidation at 100°C as well as after repeated calcinations and oxidation reactions were employed for XRD measurements to see if any change in the CoO_x species occurs and the resulting spectra were compared to those of the reference Co_3O_4 and of a sample of 5 wt% $\text{CoO}_x/\text{TiO}_2$ calcined at 350°C . All these spectra are provided in Fig. 3. An original intensity of the XRD patterns for the samples was reduced, by 30-70%, to give an easier comparison; however, all characteristic peaks were clearly visible even after such reduction. The anatase TiO_2 showed a predominant characteristic peak at a 2θ value of 25.30° , corresponding to the (101) crystalline plane, with substantial reflections at higher 2θ values (Fig. 3a). Diffraction patterns taken with the Co_3O_4 occurred at 2θ values of $18.99, 31.26, 36.84, 38.56, 44.80, 59.38$ and 65.22° , and the 36.84° peak concerning with the crystallographic (311) plane of Co_3O_4 was predominant (Fig. 3b). Additional XRD peaks due to CoO_x species in the catalyst after calcination at 350°C appeared at 2θ values of $18.99, 31.20, 36.91, 38.58, 44.81, 59.36$ and 65.21° , as indicated by the vertical dotted bars in Fig. 3c, and these peak positions were almost equal to that revealed for Co_3O_4 . Although the calcined sample underwent CO oxidation at 100°C for ca. 21 h as given in Fig. 1, no alteration was observed for XRD pattern, as shown in Fig. 3d. Furthermore, three consecutive calcinations and on-stream CO oxidation runs led to positions of Co_3O_4 peaks and their intensity very similar to that obtained for the only-calcined sample (spectrum c)

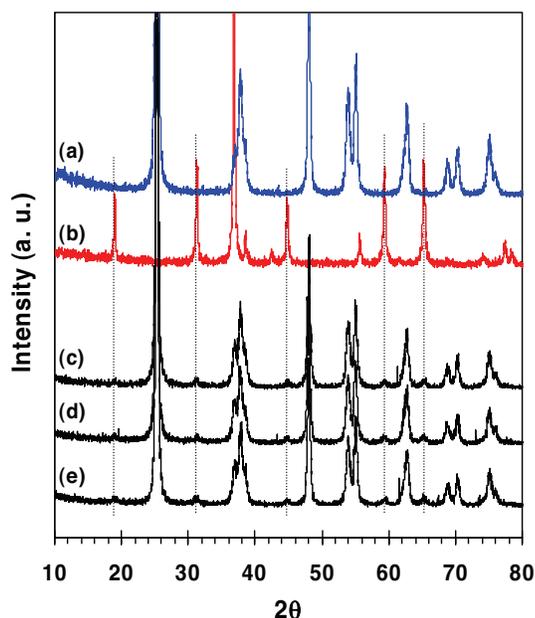


Figure 3: XRD patterns for: (a) TiO_2 ; (b) Co_3O_4 ; and (c) 5 wt% $\text{CoO}_x/\text{TiO}_2$ after calcination at 350°C (d) following a single CO oxidation at 100°C ; (e) after three repeated calcinations at 350°C and CO oxidation runs at 100°C .

The effect of O_2 concentration on the duration of the catalytic activity for CO oxidation at 100°C over 5 wt% $\text{CoO}_x/\text{TiO}_2$ calcined at 350°C , that had revealed best stability, is shown in Fig. 4 in which the preceding on-stream performances of the catalyst under a flow of 3% O_2 in He has been again included to readily allow a comparison. Practically zero activity was exhibited with purely reducing condition, but the presence of 0.5% O_2 in the feed stream gave an initial conversion of ca. 90% although this activity decreased gradually until 15 h from which steady-state conversions near 10% were observed. These results combined with the catalytic behavior obtained under 1.8 and 3% O_2 concentrations may be associated with the formation of carbonaceous substances on the catalyst surface [7-9]. The reason why the catalyst possessed poorer durability in the oxidation in the presence of 10% O_2 is uncertain, but this seems to be related to surface reconstruction [8].

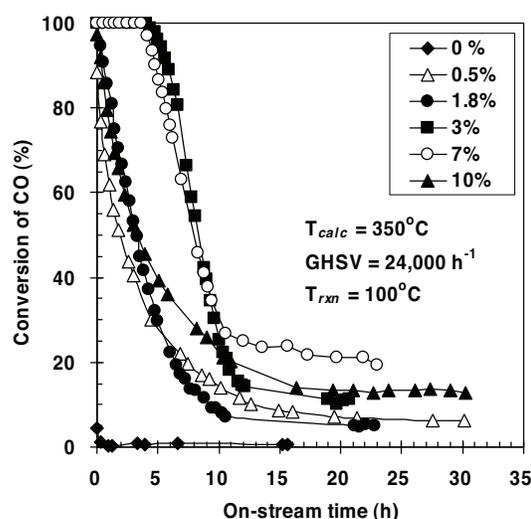


Figure 4: Activity profiles for CO oxidation at 100°C over 5 wt% $\text{CoO}_x/\text{TiO}_2$ after calcination at 350°C as a function of O_2 concentration.

The XRD measurements with all the samples employed here indicated only peaks for Co_3O_4 nanocrystallites as discussed, which was very consistent with results acquired by Raman spectroscopy, and an average crystallite size of 11 nm was obtained with a sample of 5 wt% $\text{CoO}_x/\text{TiO}_2$ after calcination at 350°C but it depended on the amounts of CoO_x loaded. The Co_3O_4 nanoparticle size was unchanged even not only after a single CO oxidation run at 100°C but also with repeated calcination and measurements.

The BET surface area for the sample in Fig. 2 was $83 \text{ m}^2/\text{g}$, which is very similar to that ($79 \text{ m}^2/\text{g}$) measured with a sample of 5 wt% $\text{CoO}_x/\text{TiO}_2$ calcined at 350°C but not used for the oxidation reaction, as listed in Table 1. No difference in the pore size distribution was also observed between the deactivated sample and the fresh one (not

shown here). An amount of residual carbonaceous species in a sample of 5 wt% CoO_x/TiO₂ after calcination at 350°C followed by a single run at 100°C was determined to be 0.38 wt% as an elemental carbon. This suggests that such deposited carbonaceous materials may be one of some possibilities causing the deactivation during the course of reaction, although further systematic studies are required later.

In an attempt to gain a better understanding of the deactivation behavior in the oxidation of CO at 100°C with 5 wt% CoO_x/TiO₂, the surface of this catalyst after undergoing the reaction under different conditions was analyzed via XPS measurements and the results are very complicated. The Co 2p XPS spectra for the catalyst sample calcined at 350°C gave a surface CoO_x phase which consists of Co₃O₄, irrespective to CoO_x loading. The O 1s binding energies in the XPS spectra with samples, which had been subjected to the CO oxidation reactions as a function of reaction parameters varied with duration impairment.

4 CONCLUSIONS

CoO_x/TiO₂ catalysts consisting of Co₃O₄ nanoparticles have noticeable difference in the durability for CO oxidation at 100°C between reaction parameters including CoO_x contents, calcination excursion and feed gas compositions. The 5 wt% CoO_x catalyst possessed best duration for the oxidation reaction. An optimal O₂ amount by 3-7% facilitates the oxidation reaction and allows a better durability, and at lower O₂ concentrations the formation of some carbonaceous species are more probable and accumulated on the catalyst surface. Not only could the deposition of carbonaceous species on the surface be associated with this complicated deactivation behavior, but surface reconstruction also seems to take place during the oxidation reaction, depending on reaction parameters.

ACKNOWLEDGEMENT

A partial grant-in-aid for the present study was provided by the Korea Research Foundation via Grant KRF-2007-314-D00039.

REFERENCES

- [1] M.H. Kim and I.S. Nam, in "Catalysis – Specialist Periodical Reports" (J.J. Spivey, Senior Reporter), Vol. 18, Chap. 4, The Royal Society of Chemistry, Cambridge, 2005.
- [2] A. Bhave, M. Kraft, F. Mauss, A. Oakley and H. Zhao, SAE Technical Paper 2005-01-0161.
- [3] J. Jansson, J. Catal. 194, 55, 2000.
- [4] K. Omata, Y. Kobayashi and M. Yamada, Catal. Commun. 6, 563, 2005.
- [5] W.H. Yang, M.H. Kim and S.W. Ham, Catal. Today, 123, 94, 2007.

- [6] K.H. Kim and M.H. Kim, in Proceedings of 2nd Internal Conference on Environmental Sciences (ICES'07), Ulaanbaator, Mongolia, 28 June-2 July, 2007, p. 106.
- [7] P. Thormahlen, M. Skoglundh, E. Fridell and B. Andersson, J. Catal. 188, 300, 1999.
- [8] J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L. Osterlund, P. Thormahlen and V. Langer, J. Catal. 211, 387, 2002.
- [9] F. Grillo, M.M. Natile and A. Glisenti, Appl. Catal. B 48, 267, 2004.