APC-LB-Topic I

Low-temperature CO oxidation for HCCI road applications

Low-temperature CO oxidation in environmental and industrial catalysis

- ❒ Engine-out emissions control for advanced vehicles with homogeneous charge compression ignition (HCCI) engines
- ❒ Reformer product purification for polymer electrolyte fuel cells
- ❒ Indoor air cleaning
- ❒ Gas sensors
- ❒ Gas masks
- ❒ Prevention of the deactivation of CO_2 lasers

The need of low-temperature CO oxidation in HCCI road applications

The 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 ($NO + NO_2$) and particulate matter (PM) emissions; therefore, HCCI engine-equipped automobiles are probably one of the most promising candidates to meet very stringent future emission standards, e.g., US Tier 2 program and EURO 5.

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%. These emissions occur at low exhaust temperatures that make it difficult to employ catalysts, such as well-proven three-way catalytic converters (TWCs), for reducing the engine-out emissions. Furthermore, the TWCs consisting of Rh, Pt and Pd as major active moieties would not be available for HCCI applications because of high concentrations of O_2 in the exhaust which can readily transform the Rh to an inactive Rh_2O_3.

Requirements for HCCI road applications

◆ HCCI combustion technology:

- has high thermal efficiencies, comparable to diesel engines;
- gives dramatic reduction in NO_x and particulate matter (PM) emissions;
- meets very stringent future emission standards (US Tier 2 and EURO 6).

◆ One of the current challenges to the HCCI technology is:

- reduction in CO and HCs emissions.

◆ Well-proven three-way catalytic converters (TWCs):

- would not be available for HCCI engine-out emissions control because of high concentrations of O_2 in the exhaust.

Simulated conditions for HCCI applications

Gas composition and operating temperature window	HCCI	PEMFC
CO (%)	> 1	0.5 ~ 2
H_2 (%)	n.d.	45 ~ 75
CO_2 (%)	n.d.	15 ~ 25
H_2O (%)	n.d.	15 ~ 30
NO_x (ppm)	< 20	n.d.
HC[a] (%)	> 1	trace
PM (mg/m^3)	≈ 0[b]	n.d.
T (^oC)	r.t. ~ 280	70 ~ 300

[a] Unconverted or burned.

[b] Under detection limits.

Representative catalysts for low-temperature CO oxidation

❐ **Supported precious noble metals, such as Pt, Rh, Pd, Ru, and Ir**

- **high performances and stability**
- **key constituents in automotive catalysis**

❐ **Supported Au nanoparticles**

- **very high activity even at temperatures as low as -70°C**
- **nanosized gold particles (< 10 nm) dispersed uniformly on transition metal oxides**

The need to substitute for the supported platinum group metals-based and Au catalysts is because of the high cost of precious metals and their weak sulfur tolerance.

❐ **Supported or promoted CuO systems**

- **CuO-CeO_2 mixed oxides: highly active and exceptionally selective with a PrO_x condition**
- **Unpromoted and unsupported CuO: complete oxidation even at ambient temperatures**

❐ **Unsupported and supported CoO_x catalysts**

- **Unsupported Co_3O_4 powders: highly active at temperatures greater than 150°C, depending significantly on calcination temperatures**
- **Supported cobalt oxides: dependent on supports and pretreatment procedures used**

Keypoints to candidate good catalysts

One of the noteworthy differences in conditions between PEMFC and HCCI applications is the high concentration of H_2. Co_3O_4 gave no activity for H_2 oxidation at low temperatures, such as 130°C, when using a flowing mixture of CO, H_2 and O_2 in N_2. Compared to the CoO_x dispersed on SiO_2 and Al_2O_3, CoO_x/TiO_2 catalysts were very difficult to reduce while flowing pure H_2, even at 300°C. This suggests CoO_x species that are active for CO oxidation at low temperatures, e.g., Co_3O_4, may be much more stable on TiO_2 surfaces, even in the presence of H_2.

Preparation and characterization of CoO_x/TiO_2 catalysts for low-temperature CO oxidation

❒ Preparation of CoO_x/TiO_2 catalysts *via* a wet impregnation technique

- Supports: pellet-type TiO_2 (Millennium Chemicals, DT51D, S.A. = 38 m^2/g)
  pure powder-type TiO_2 (Millennium Chemicals, DT51D, S.A. = 87 m^2/g)
- Calcination temperatures: 250, 350, 450, 510 and 570°C

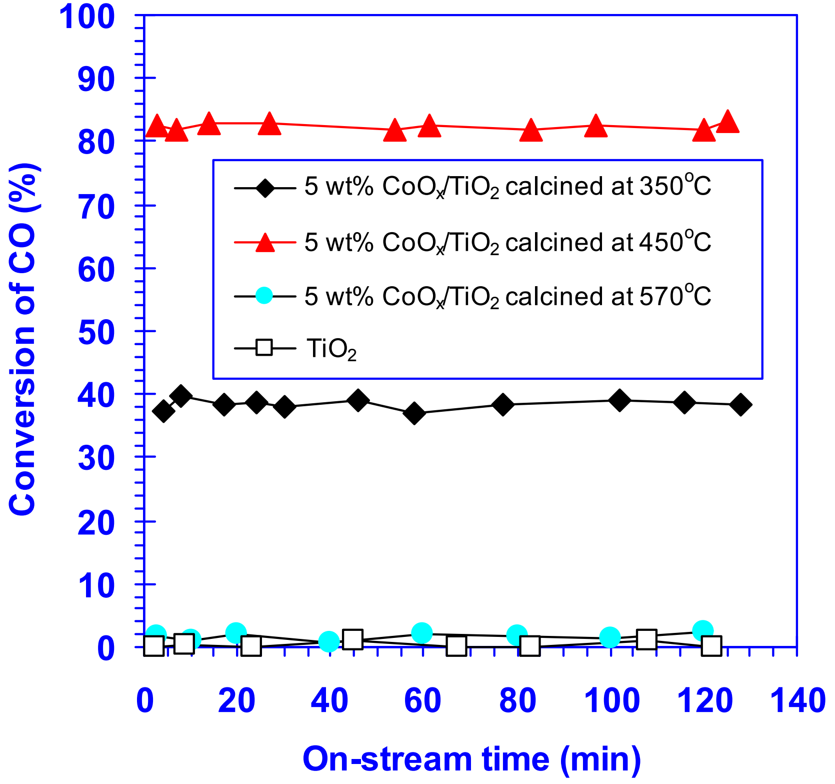
❒ Characterization for catalyst samples

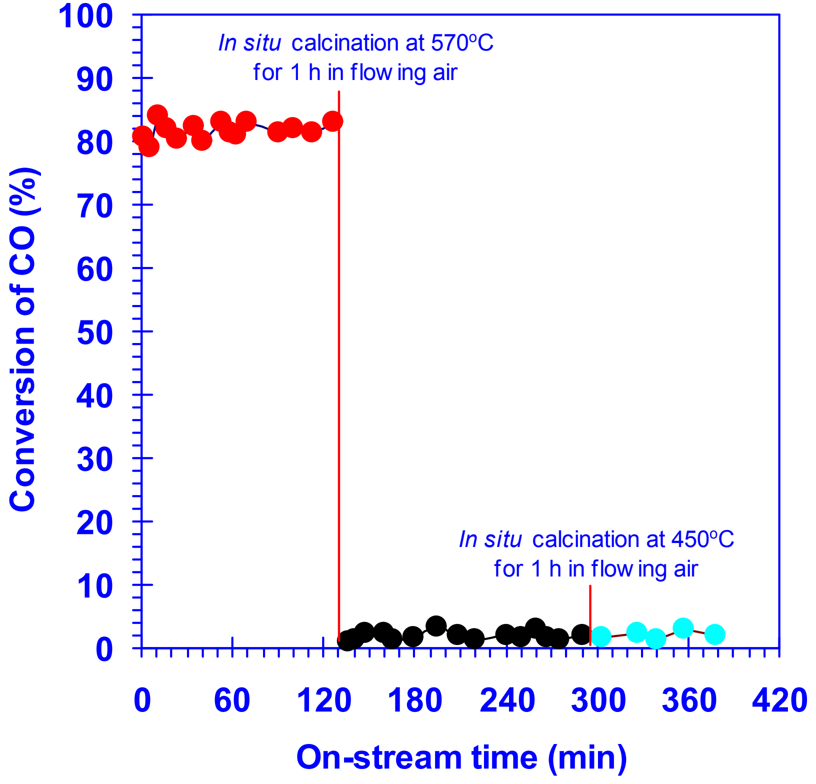
- XRD measurements for 5 wt% CoO_x/TiO_2 calcined at different temperatures
- Determination of Co 2p binding energy for the samples used for XRD measurements

❒ Catalytic CO oxidation in a continuous flow reactor system

- [CO] = 1% in a flowing mixture of 3% O_2/96% He
- $T = 100°C$
- GHSV = 6,000 – 66,000 h^{-1}

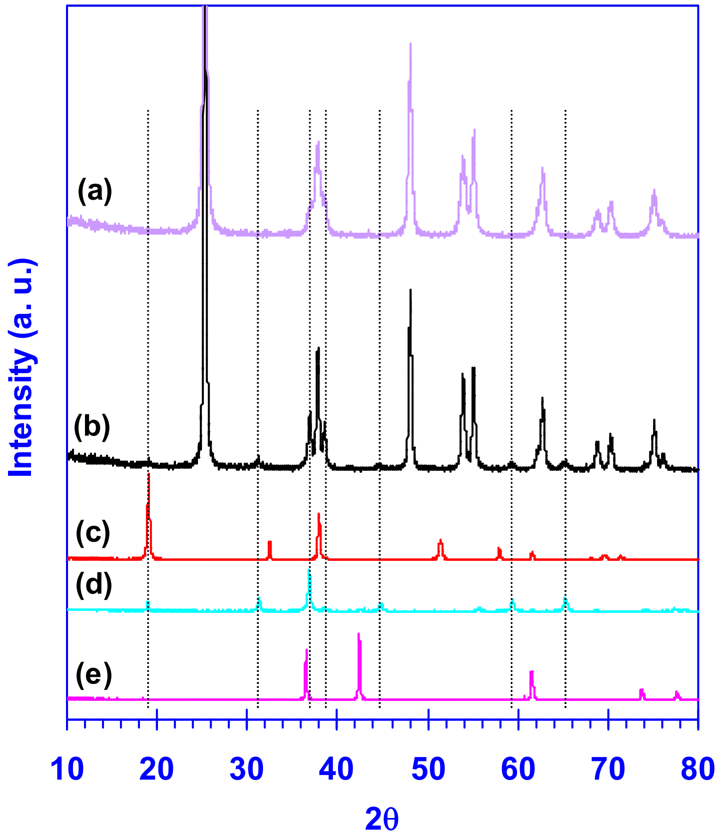
Activity profiles for CO oxidation over 5 wt% CoO_x/TiO_2 catalysts after calcination at different temperatures



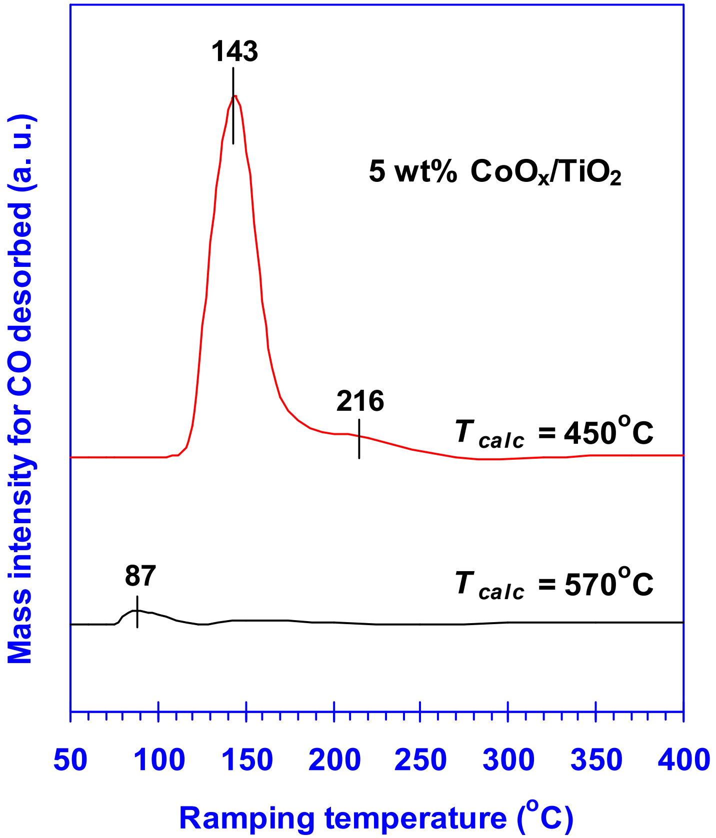


$[CO] = 1\%$, $T = 100^{o}C$, $GHSV = 66{,}000\ h^{-1}$

XRD and XPS spectra for reference Co compounds, and 5 wt% CoOx/TiO_2 calcined at different temperatures

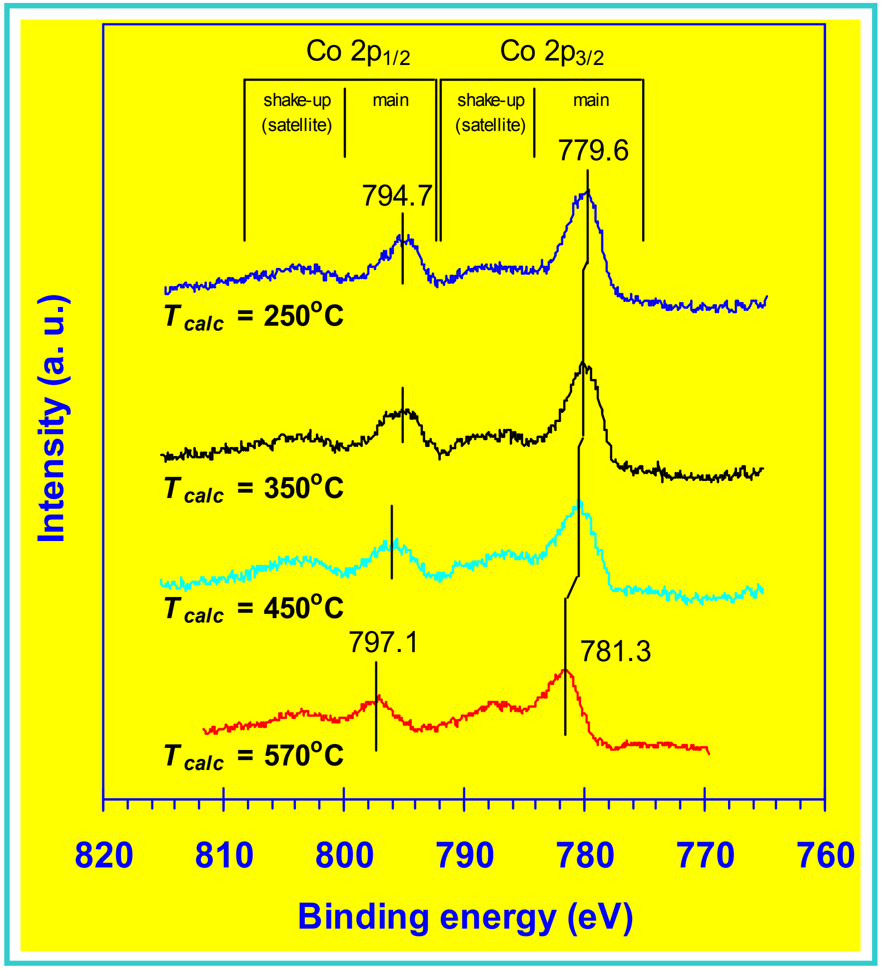


(a) TiO_2; (b) 5% CoO_x/TiO_2 calcined at 450°C; (c) $Co(OH)_2$; (d) Co_3O_4; (e) CoO. The vertical dotted bars represent the diffraction peaks for Co_3O_4.

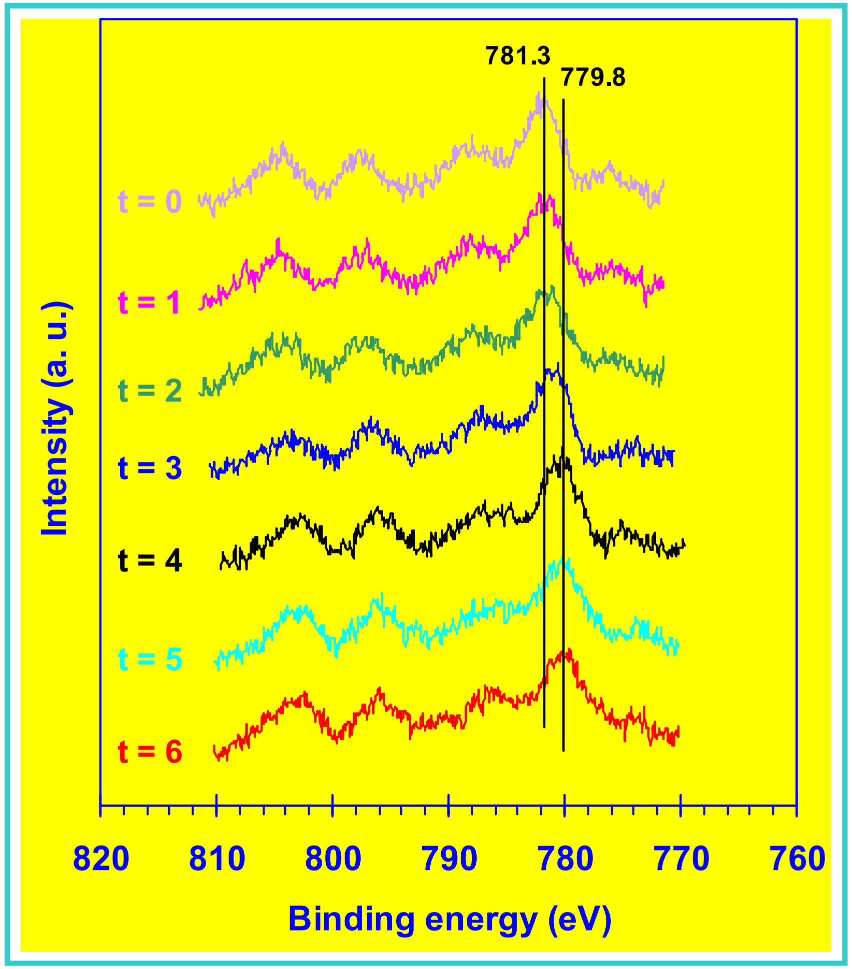


Co 2p XPS spectra for CoO_x/TiO_2 catalysts

Samples of 5 wt% CoO_x/TiO_2 calcined at different temperatures



A sample of 5 wt% CoO_x/TiO_2 calcined at 570°C following Ar^+ sputtering at a rate of 1.5 nm/min

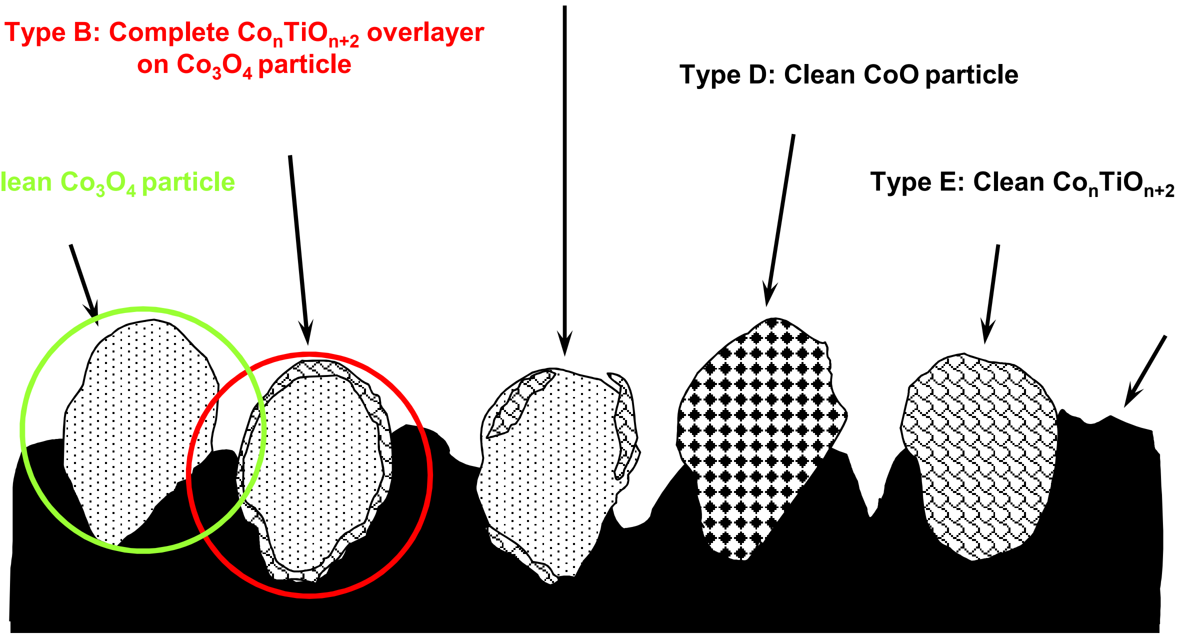


Co $2p_{3/2}$ binding energies for CoO_x/TiO_2 catalysts calcined at different temperatures

Catalyst	Calcination at:	Binding energy (eV)	ΔE[a)]
CoO	-	780.3	15.9
Co_3O_4	-	779.9	15.2
$Co(OH)_2$	-	781.2	16.0
Co_2TiO_4	-	781.1	15.7
$CoTiO_3$	-	781.3	16.0
5 wt% CoO_x/TiO_2	250°C	779.6	15.1
5 wt% CoO_x/TiO_2	350°C	779.8	15.2
5 wt% CoO_x/TiO_2	450°C	780.3	15.4
5 wt% CoO_x/TiO_2	570°C	781.3	15.8

a) Spin-orbit splitting.

Model nanoparticles for the CoO_x species with 5 wt CoO_x/TiO_2 catalysts after calcination at different temperatures



Type C: Partial Co_nTiO_{n+2} overlayer on Co_3O_4 particle

Type B: Complete Co_nTiO_{n+2} overlayer on Co_3O_4 particle

Type D: Clean CoO particle

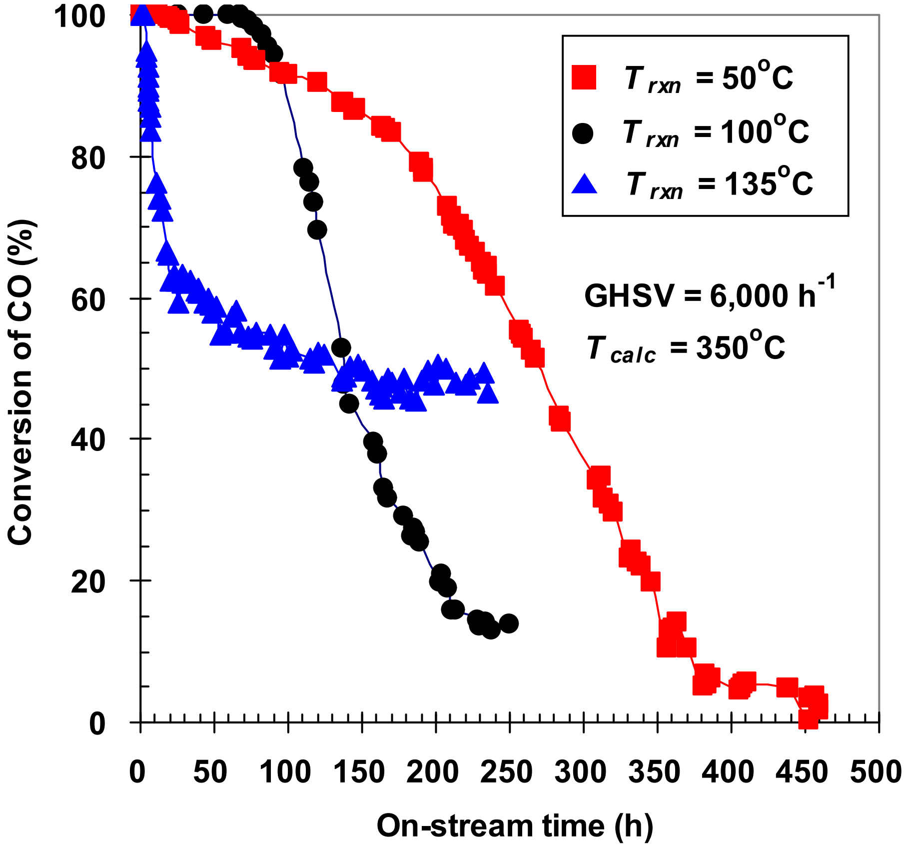
Type A: Clean Co_3O_4 particle

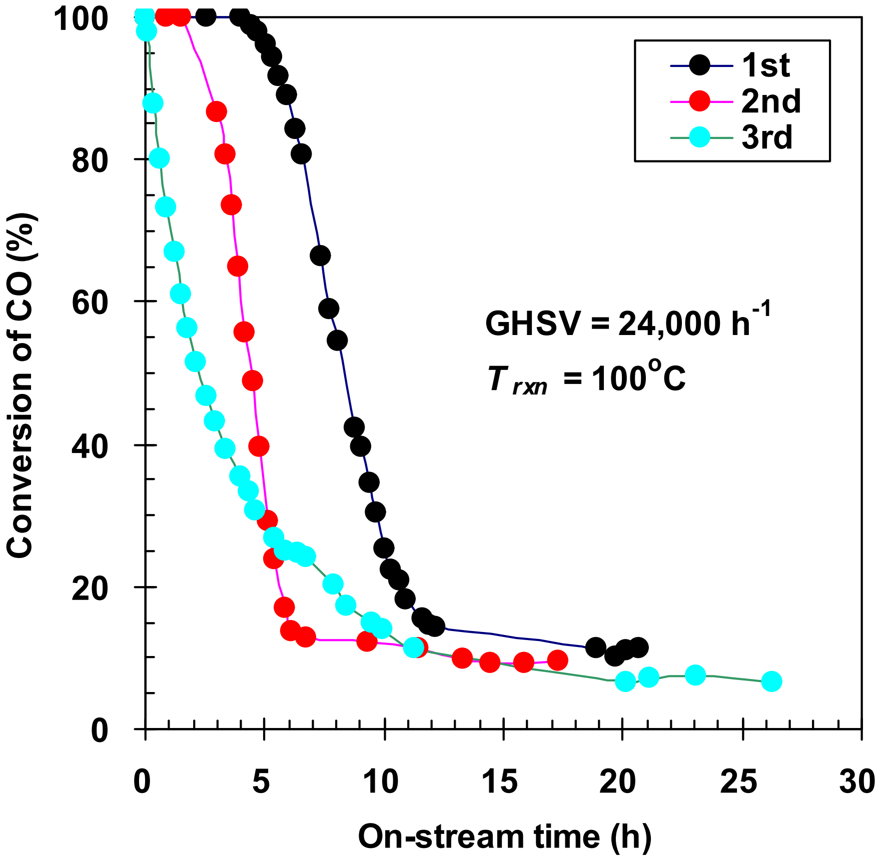
Type E: Clean Co_nTiO_{n+2} particle

TiO_2

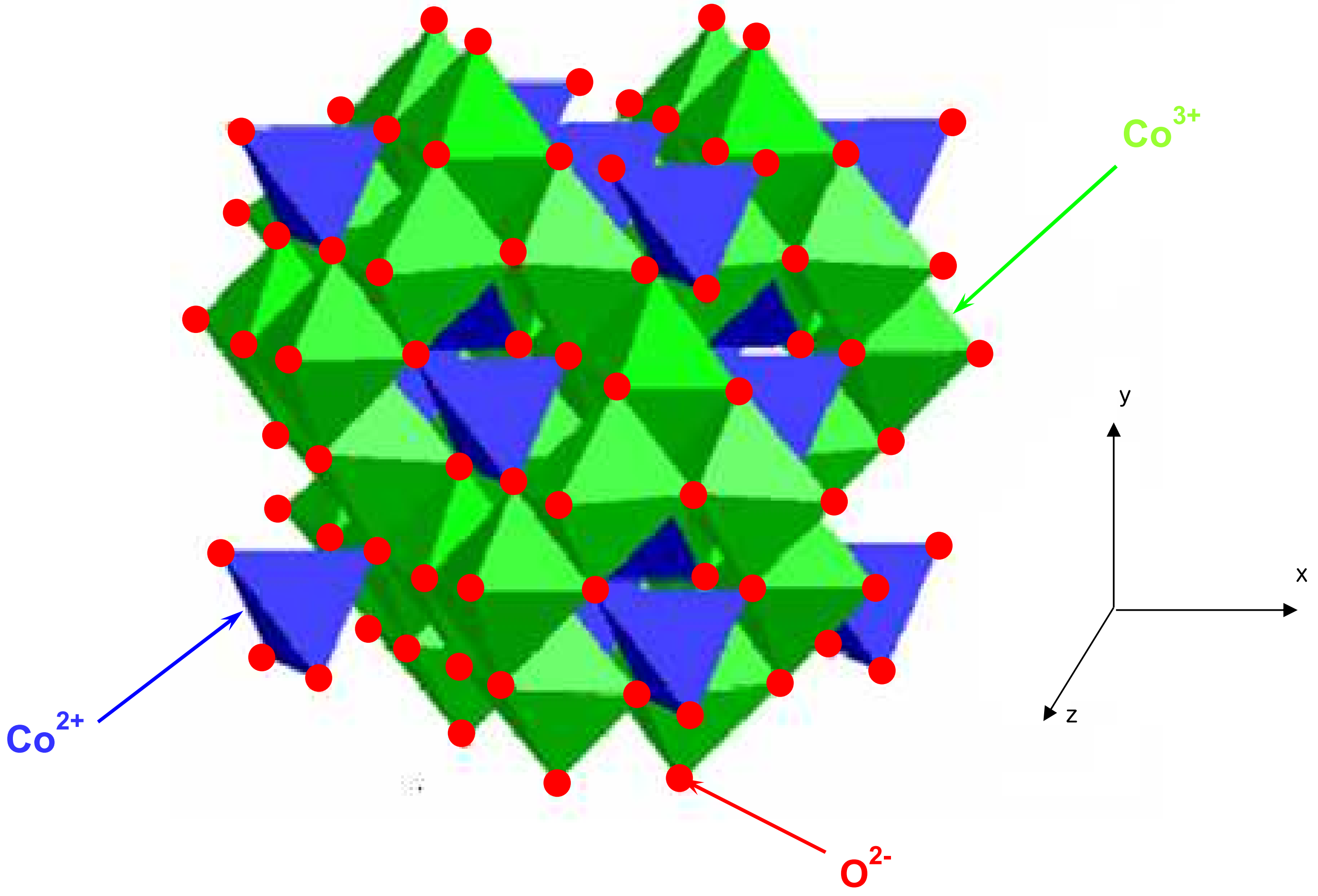
Consequently, a 5% CoO_x/TiO_2 catalyst calcined at 570°C possesses the Type B, but calcining it at 450°C gives the Type A Co_3O_4 nanoparticles.

Durability of 5 wt% CoO_x/TiO_2 calcined @ 350°C for CO oxidation at different temperatures

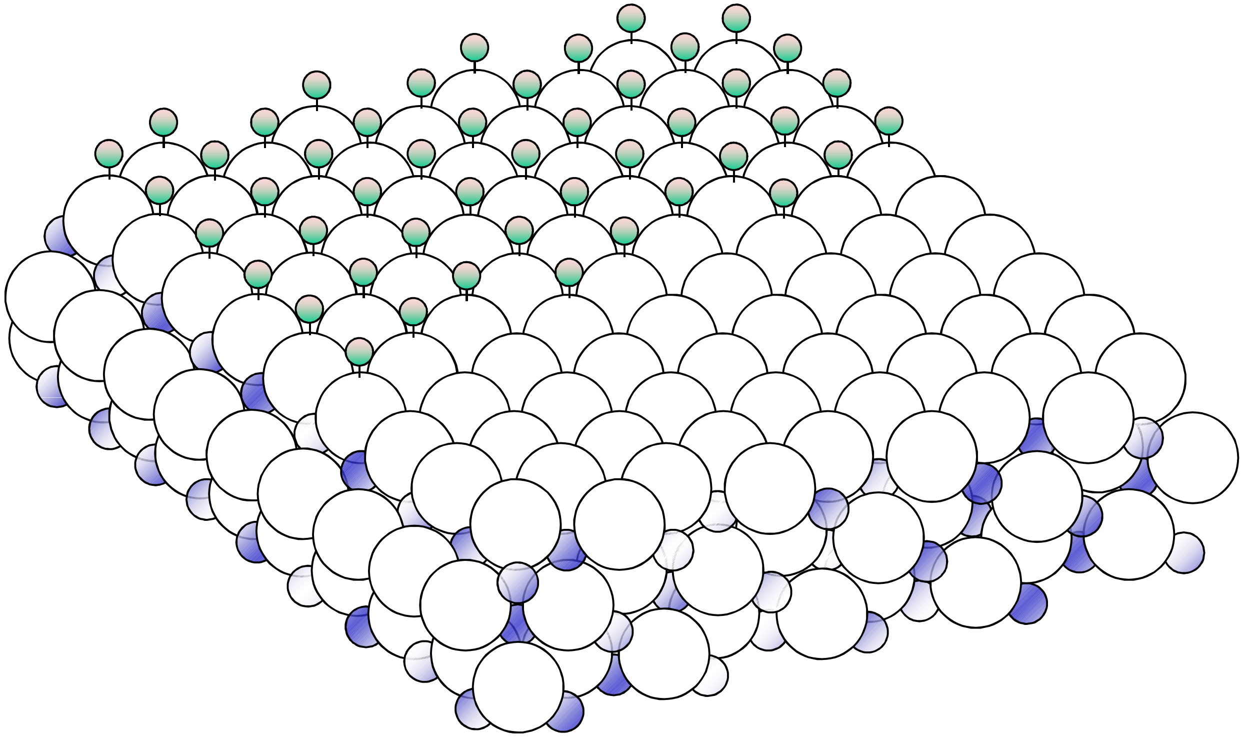




Structure of Co_3O_4



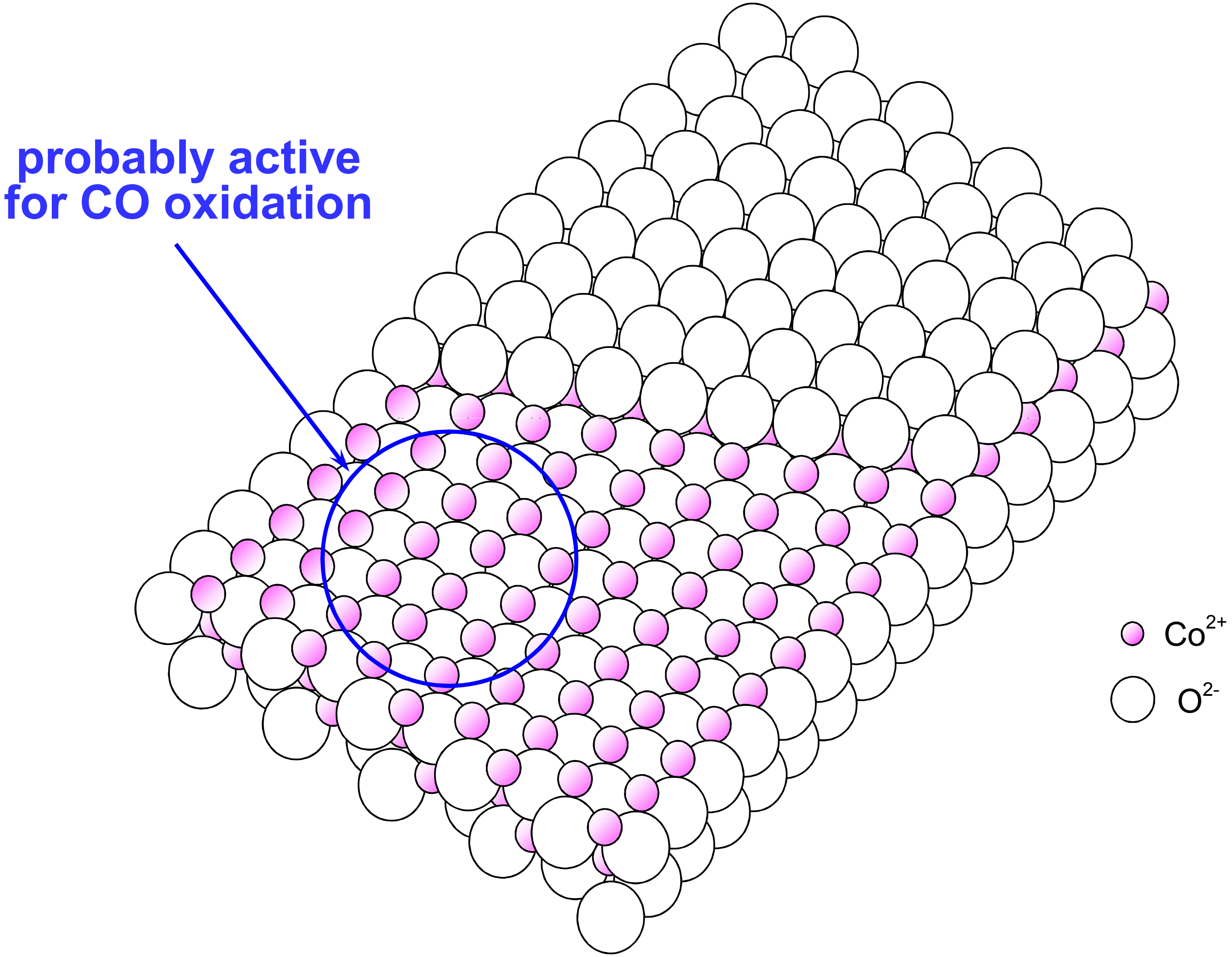
OH- and O-terminated CoO_x surface



This surface:

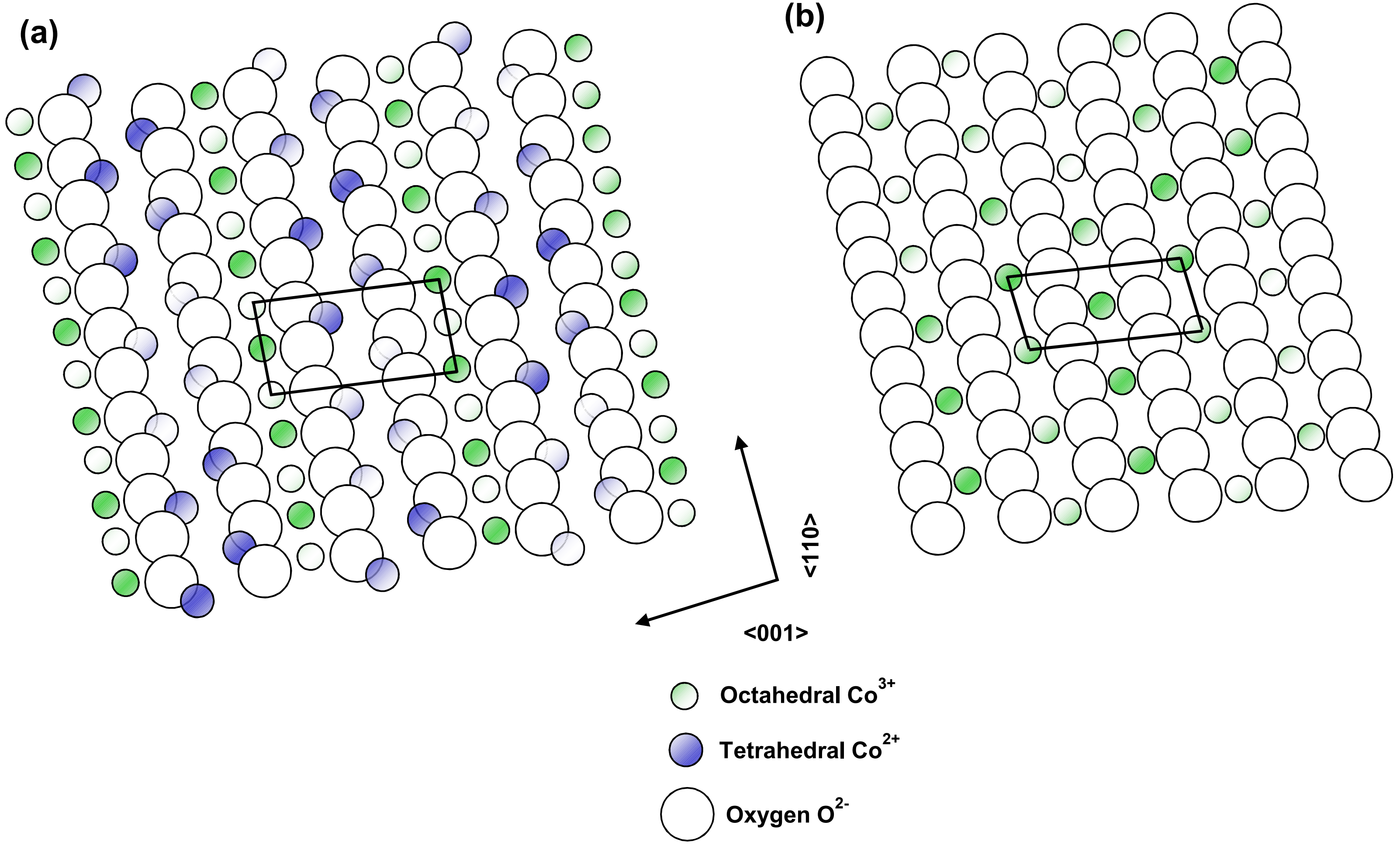
- **may not be not active for CO oxidation reaction;**
- **may not be probable.**

Unreconstructed CoO$_x$ surface

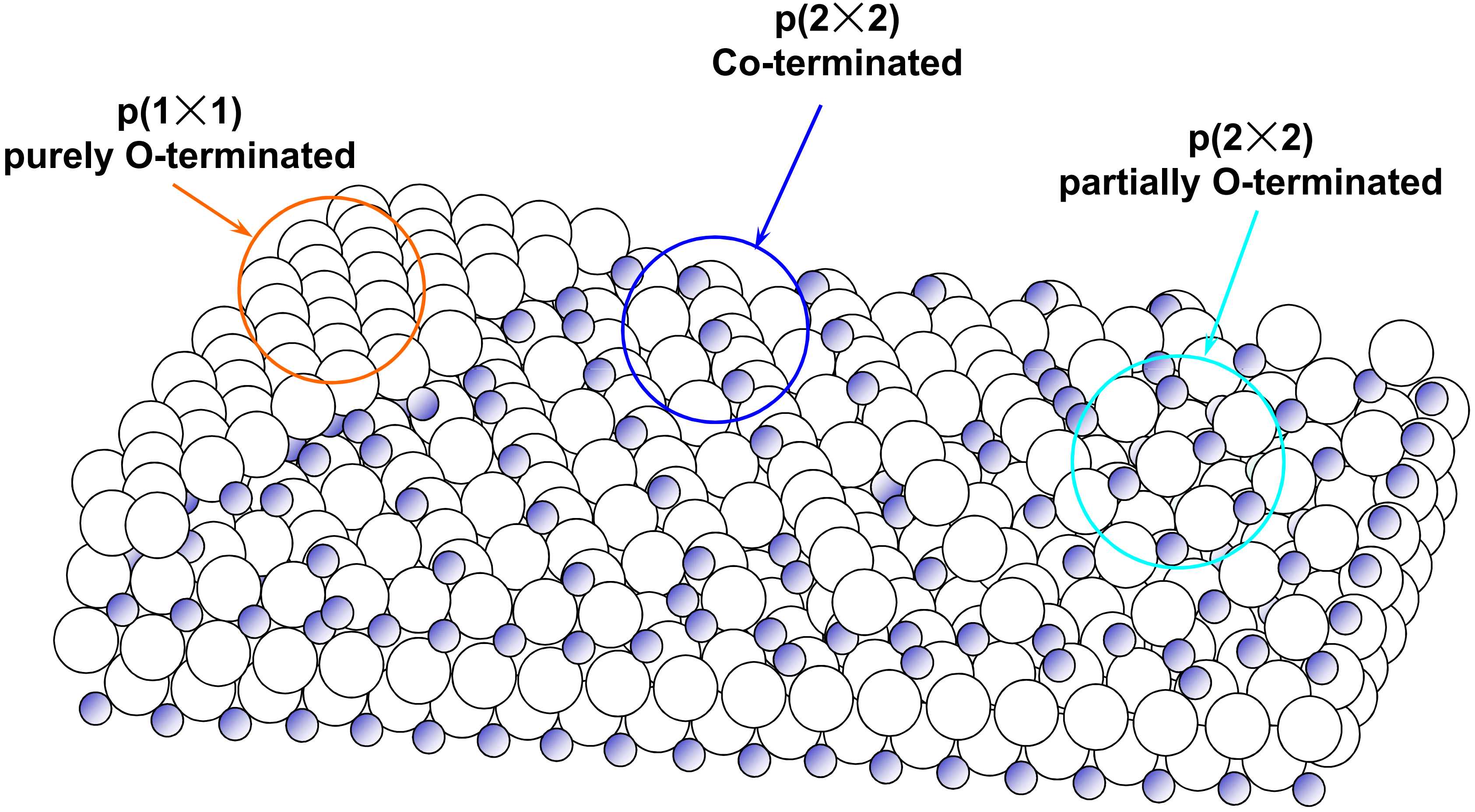


probably active for CO oxidation

Bulk termination planes of Co_3O_4



Octopolar reconstructed CoO_x surface



p(2×2)
Co-terminated

p(1×1)
purely O-terminated

p(2×2)
partially O-terminated

Catalysts and system used for CO oxidation

❒ **Preparation of CoO_x/TiO_2 catalysts *via* a wet impregnation technique**

- **Supports: pure powder-type TiO_2 (Millennium Chemicals, DT51D, S.A. = 87 m^2/g)**

❒ **Synthesis of Co_nTiO_{n+2} *via* a solid-state reaction**

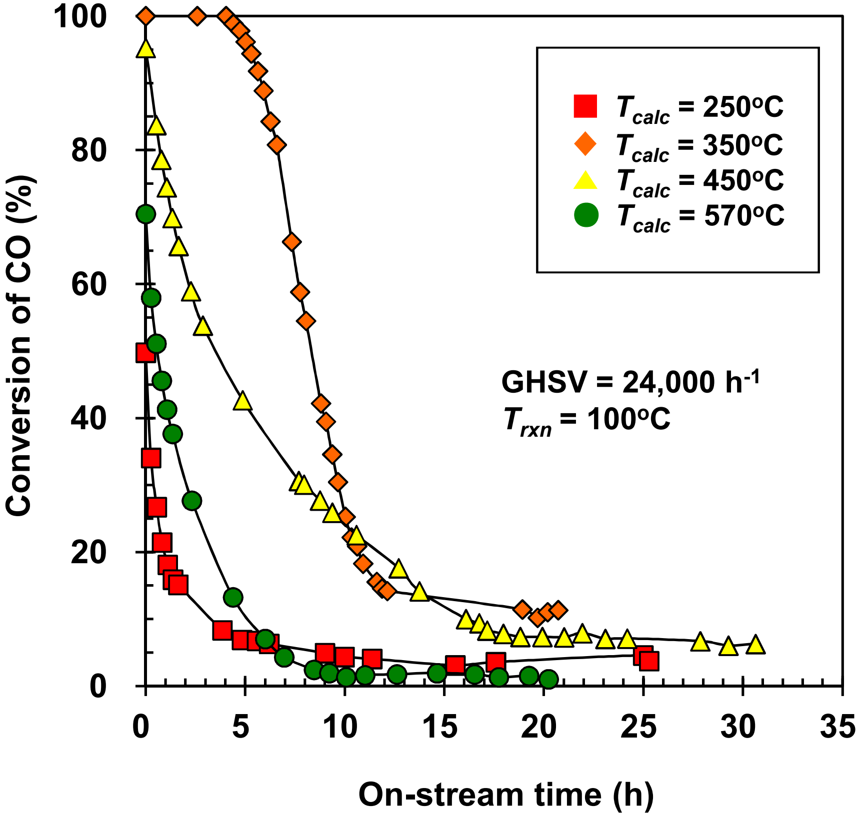
- $CoO + TiO_2 \rightarrow CoTiO_3$
- $2CoO + TiO_2 \rightarrow Co_2TiO_4$

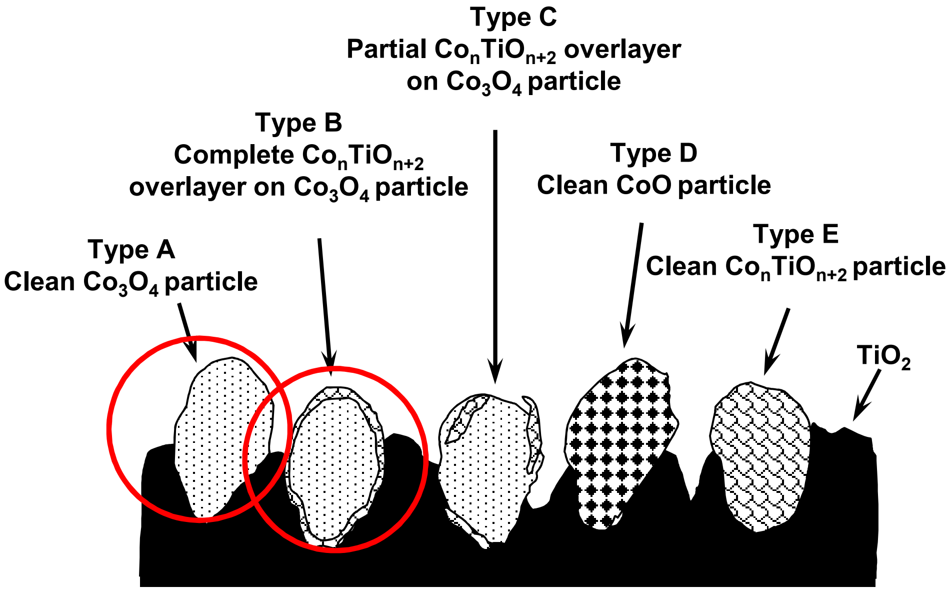
❒ **Catalytic CO oxidation using a continuous flow reactor system**

- **1% CO in a flowing mixture of 3% O_2/96% He**
- **Reaction temperature = 100 – 180°C, hereafter designated to T_{rxn}**
- **Calcination temperature = 250 – 570°C, hereafter designated to T_{calc}**
- **GHSV = 6,000 – 24,000 h^{-1}**

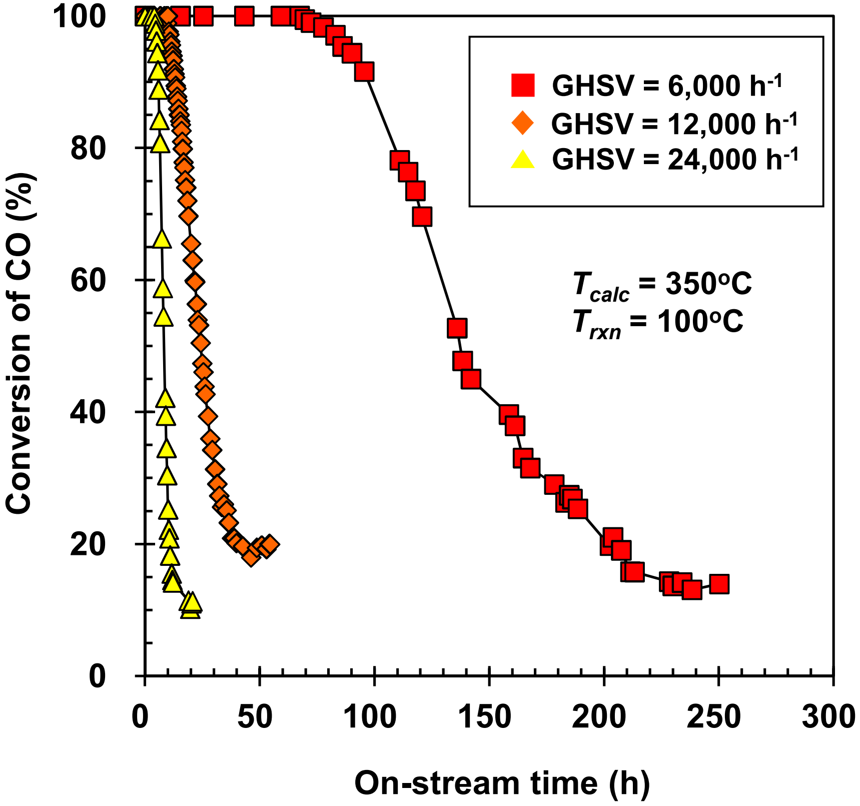
CO oxidation over 5% CoO_x/TiO_2

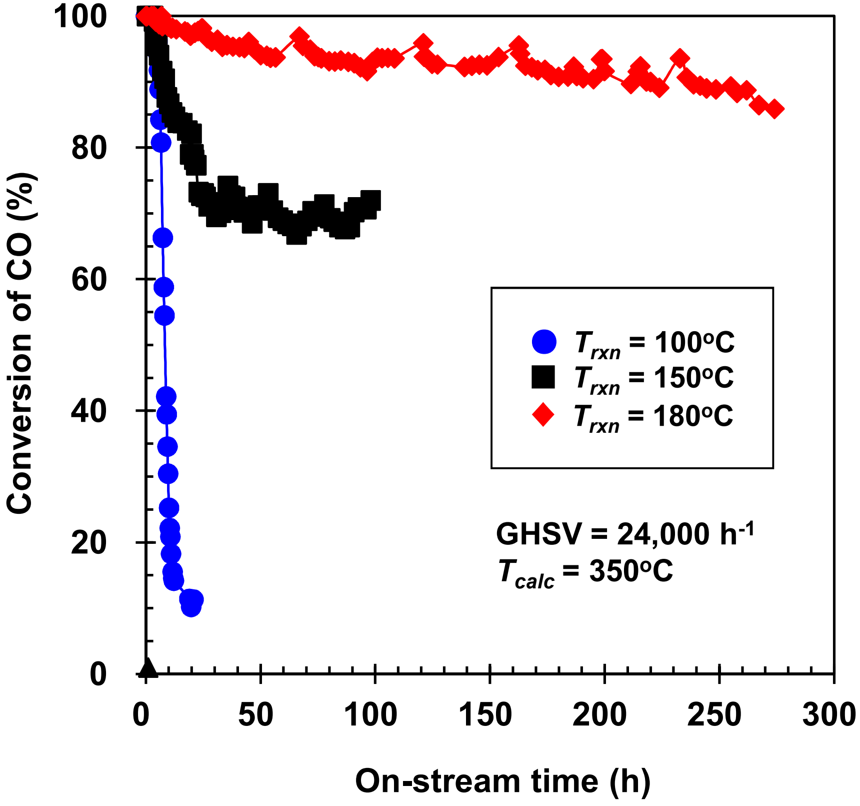
Effect on calcination excursion and an earlier proposed model for CoO_x





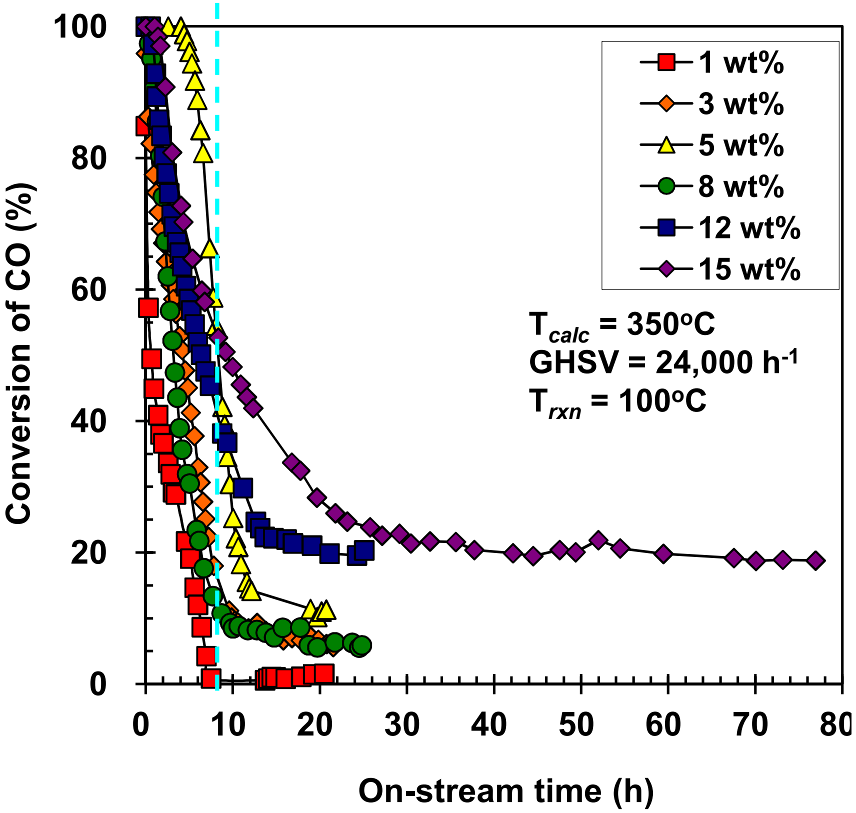
Effect on GHSVs and T_{rxns}

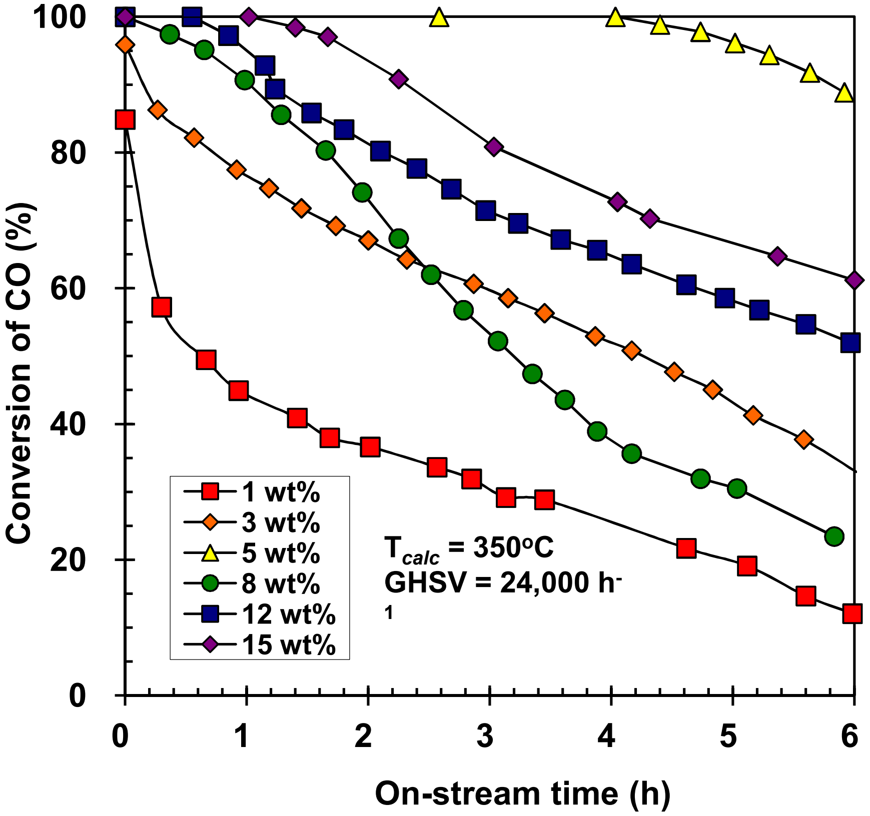




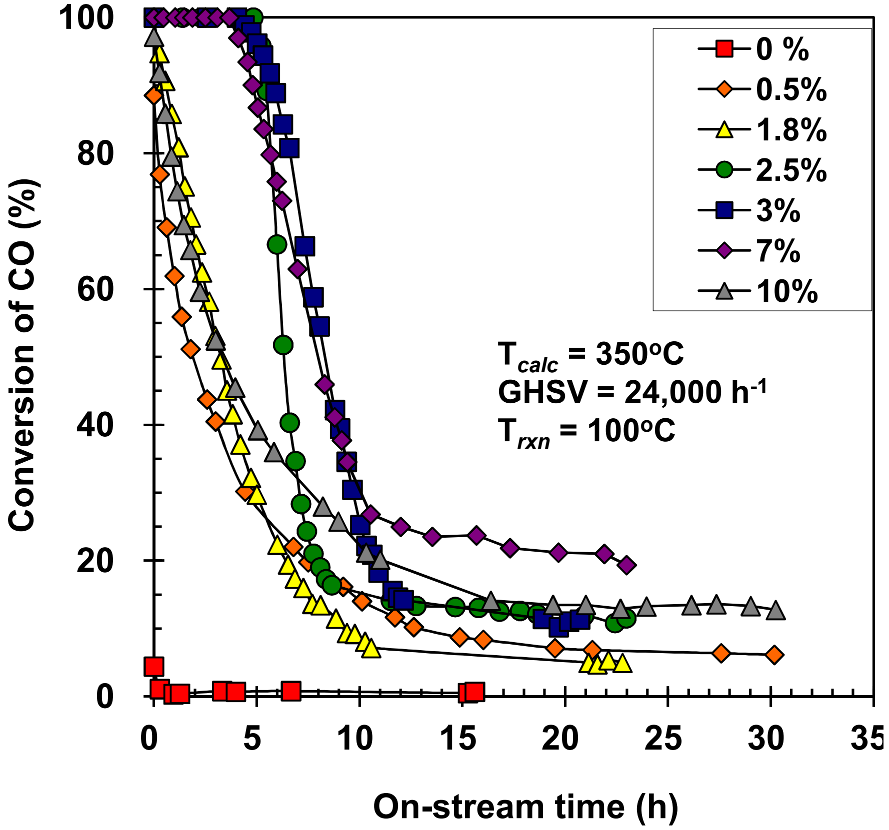
Effect on CoO_x amounts

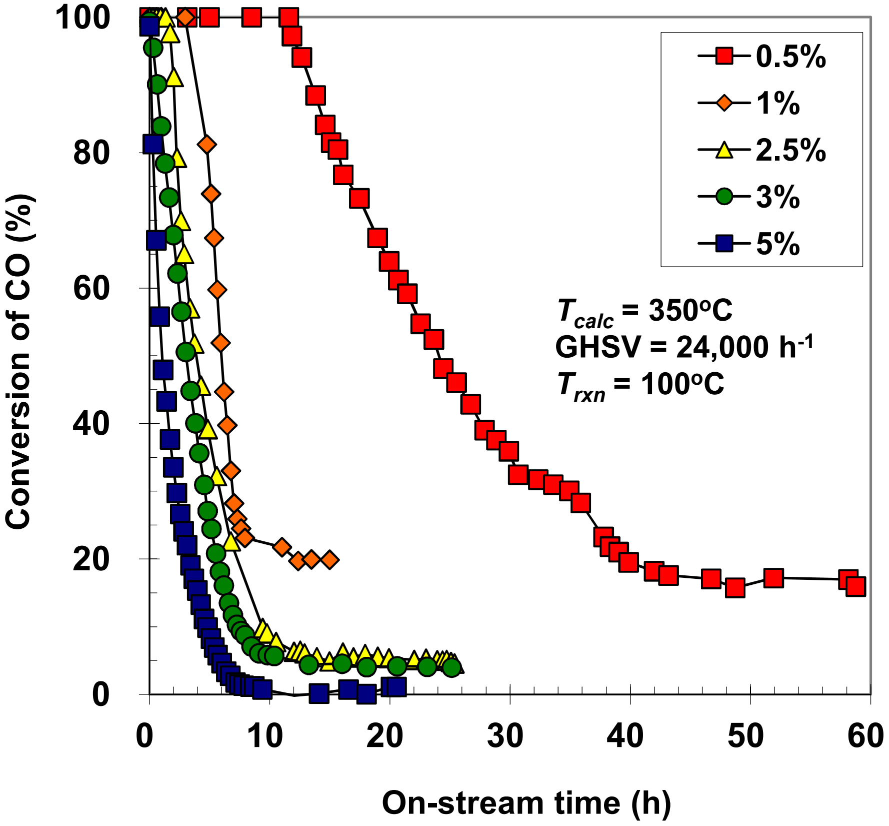
See the right-side figure for the activity profiles up to this on-stream hours.





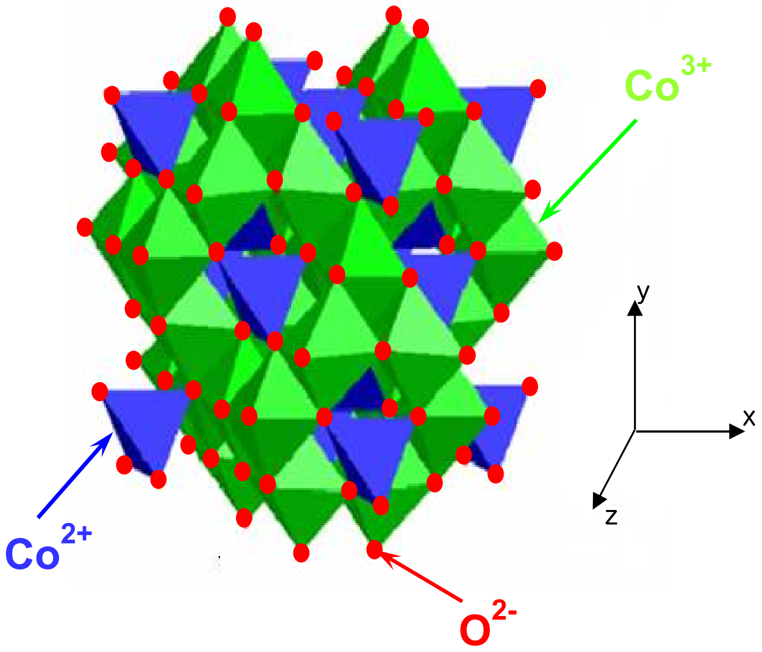
Effect on O_2 and CO concentrations



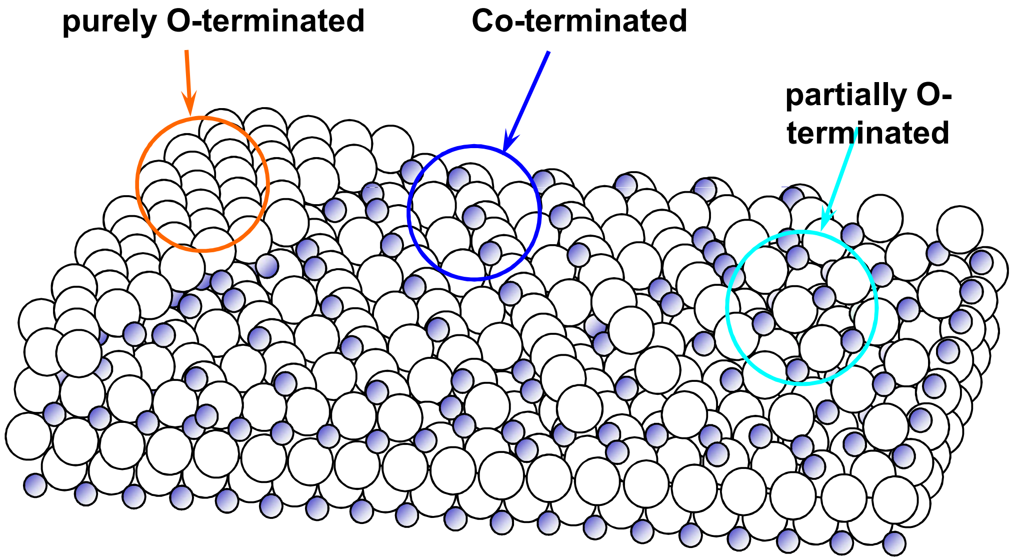


Octopolar CoO_x surface

Surface reconstruction of Co_3O_4



Structure of Co_3O_4



Summary

- A 5% CoO_x/TiO_2 catalyst:

  - is quite active for CO oxidation even at low temperatures; but
  - exhibits very complicated behavior in duration of its activity for this reaction.

- Durability of the catalyst in CO oxidation at 100°C depends significantly on:

  - thermal excursion and reaction parameters.

- Such deactivation behavior is probably associated with:

  - surface reconstruction;
  - the deposition of carbonaceous materials.