MATERIALS AND METHODS

Materials

1. Reagents

- Lanthanum (III) nitrate hexahydrate [$La(NO_3)_3.6H_2O$, 99%, BDH]
- Cobalt (II) nitrate hexahydrate [$Co(NO_3)_2.6H_2O$, 99%, Univar]
- Citric acid ($C_6H_8O_7.H_2O$, 99%, Merck)
- Ethylene glycol ($C_2H_4(OH)_2$, 98.0%, Fluka)
- Salicylaldehyde ($C_7H_6O_2$, 98.0%, Fluka)
- Ethylenediamine ($C_2H_4(NH_2)_2$, 99.0%, Fluka)
- Ammonia solution (NH_4OH, 25.0%, Fisher Chemicals)
- Toluene ($C_6H_5CH_3$, 99.5%, Carlo Erba)
- Oxygen (O_2, 99.999%, Thai Industrial Gases)
- Nitrogen (N_2, 99.999%, Thai Industrial Gases)
- Argon (Ar, 99.999%, Thai Industrial Gases)

2. Instruments

- Acidity measurements were performed on a AB10 Bench pH/MV meter.
- All prepared catalysts were calcined in a Thermolyne 2100 tube furnace using a quartz tube.
- Decomposition precursors were characterized by a TGA 7 Perkin Elmer.
- Infrared spectra were obtained using a System 2000 FTIR Perkin Elmer spectrometer.
- Structural morphology was performed on a Philips X’ Pert x-ray diffractometer using Cu K_α radiation (λ 1.54 Å). The crystalline phase of samples was identified by using the Joint Committee on Powder Diffraction Standards (JCPDS) files.

- Elemental analyses for determining of elemental mole ratio in a unit cell were obtained using a Philips PW2400 x-ray fluorescence spectrometer. The SemIQ analytical program was used as the reference material standard.

- Oxidation state determination was performed on an x-ray photoelectron spectrometer. The spectra were obtained on VG Scientific system equipped with a Thermo VG Scientific x-ray source and a VG Scientific concentric hemispherical analyzer operated at 50 eV constant pass energy using Al K_α (1486.68 eV) radiation at 400 watt. The experiment was carried out at Siam Photon Laboratory.

- Surface areas of catalysts were obtained by the BET method from nitrogen adsorption isotherms, recorded at 77 K on a Micromeritics ASAP 2020 instrument.

- The catalytic activity was tested in a Specac environmental chamber. Toluene was introduced into a vaporizer (423 K) by a peristaltic pump (Masterflex). Toluene and adsorbed compounds during the oxidation reaction were analyzed *in-situ* by DRIFTS (Bruker vector 33) using Mercury-Cadmium-Telluride (MCT) detector and KBr beam splitter. Spectra were collected with a resolution of 4 cm^{-1} using 32 scan averages recording every minute.

Methods

1. Catalyst Preparation

$LaCoO_3$ perovskite-type was synthesized by three different methods: the Pechini method, Schiff base complex method and coprecipitation.

1.1 The Pechini method

$Co(NO_3)_2 \cdot 6H_2O$ (0.3000 M, 25.00 cm^3) was mixed with citric acid in a mole ratio of 1:3. $La(NO_3)_3$ (0.3000 M, 25.00 cm^3) was added to the mixture. The mixture was stirred and slowly heated to 363 K followed by addition of ethylene glycol in a mole ratio of 40: 60 with respect to citric acid. The mixture was stirred for 3 hours to accelerate polyesterification reaction of citric acid and ethylene glycol, and then heated at 363 K to remove excess solvent and to polymerize providing resin which are dried at 383 K for 12 hours and was assigned as LC-PN.

The reference gel was prepared by the method as described above without adding any metal precursors and was assigned as PN. Gel with lanthanum-precursor was prepared by the method as described above with the addition of $La(NO_3)_3$ precursor only and was assigned as La-PN. Gel with cobalt-precursor was prepared by the method as described above with the addition of $Co(NO_3)_2$ precursor only and was assigned as Co-PN.

Heating steps for calcination of the dried sample were set as follows:

- The first step: the temperature was increased from room temperature to 473 K and held for 2 hours with flowing N_2 of 50 cm^3min^{-1},
- The second step: the temperature was raised to 623 K with flowing N_2 of 70 cm^3min^{-1} and O_2 of 30 cm^3min^{-1}.
- The last step: the temperature was heated up to 973 K with flowing N_2 and O_2 of 50 cm^3min^{-1} each. The ramp rate of all process was 1.7 $Kmin^{-1}$.

Preparations of $LaCoO_3$ for FTIR study were the same as that described above with the exception that the calcination temperatures were step up to 973 K and held for 3 or 8 hours.

Preparations of $LaCoO_3$ for XRD were the same as that described above with the exception that the samples were calcined at 573 K, held for 3 hours and at 773, 823 and 973 K, held for 8 hours. Sample codes of the catalysts prepared by the Pechini method according to the heating conditions were assigned as shown in Table 5.

Table 5 Sample codes of the catalysts prepared by the Pechini method according to heating conditions

Sample	Heating temperature (K)	Hold up time (h)	Sample code
PN	383	12	PN383-12
La-PN	383	12	La-PN383-12
Co-PN	383	12	Co-PN383-12
LC-PN	383	12	LC-PN383-12
LC-PN	423	3	LC-PN423-03
LC-PN	473	3	LC-PN473-03
LC-PN	523	3	LC-PN523-03
LC-PN	573	3	LC-PN573-03
LC-PN	623	3	LC-PN623-03
LC-PN	773	3	LC-PN773-03
LC-PN	773	8	LC-PN773-08
LC-PN	823	3	LC-PN823-03
LC-PN	873	3	LC-PN873-03
LC-PN	973	8	LC-PN973-08

1.2 Schiff base complex method

$Co(NO_3)_2{\cdot}6H_2O$ (0.3000 M, 25.00 cm^3) was mixed with salicylaldehyde in a mole ratio of 1:6. $La(NO_3)_3$ (0.3000 M, 25.00 cm^3) was added to the mixture. The mixture was stirred and slowly heated to 328 K followed by addition of ethylenediamine in a mole ratio of 40: 60 with respect to salicylaldehyde. The mixture was stirred for 3 hours to accelerate condensation reaction of salicylaldehyde and ethylenediamine, and then heated at 338 K to remove excess solvent and to polymerize providing resin. After drying at 383 K, the dried gel LC-SB was formed. The reference gel was prepared by the method as described above without adding any metal precursors and was assigned as SB. Gel with lanthanum-precursor was prepared by the method as described above with the addition of $La(NO_3)_3$ precursor only and was assigned as La-SB. Gel with cobalt-precursor was prepared by the method as described above with the addition of $Co(NO_3)_2$ precursor only and was assigned as Co-SB.

Heating steps for calcination of the dried sample were set as follows:

- The first step: the temperature was increased from room temperature to 423 K and held at this temperature for 1 hour. The whole process was carried out under flowing N_2 of 50 cm^3min^{-1},
- The second and third steps: the temperatures were increased to 473 and 523 K, respectively, and controlled with the same method as that described in the first step.
- The fourth step: the temperature was increased to 623 K with the flowing N_2 and O_2 of 70 and 30 cm^3min^{-1}, respectively.
- The last step: the temperature was increased to 973 K and held for 8 hours under the flowing N_2 and O_2 of 50 cm^3min^{-1} each. The heating ramp rate 1.7 $Kmin^{-1}$ was used for all heating steps.

Preparations of $LaCoO_3$ for FTIR study were the same as that described above with the exception that the calcination temperatures were step up to 973 K for 3 or 8 hours.

Preparations of $LaCoO_3$ for XRD were the same as that described above with the exception the samples were calcined at 573 K, held for 3 hours and at 773, 823 and 973 K, held for 8 hours. Sample codes of the catalysts prepared by Schiff base complex method according to the heating conditions were assigned as shown in Table 6.

Table 6 Sample codes of the catalysts prepared by Schiff base complex method according to heating conditions

Sample	Heating temperature (K)	Hold up time (h)	Sample code
SB	383	12	SB383-12
La-SB	383	12	La-SB383-12
Co-SB	383	12	Co-SB383-12
LC-SB	383	12	LC-SB383-12
LC-SB	423	3	LC-SB423-03
LC-SB	473	3	LC-SB473-03
LC-SB	523	3	LC-SB523-03
LC-SB	573	3	LC-SB573-03
LC-SB	623	3	LC-SB623-03
LC-SB	773	3	LC-SB773-03
LC-SB	773	8	LC-SB773-08
LC-SB	823	3	LC-SB823-03
LC-SB	873	3	LC-SB873-03
LC-SB	973	8	LC-SB973-08

1.3 Coprecipitation

Perovskite catalysts were prepared from $La(NO_3)_3.6H_2O$, $Co(NO_3)_2.6H_2O$ with ammonium hydroxide (NH_4OH) as precipitating agent shown in equation 14.

$$La(NO_3)_3 + Co(NO_3)_2 + 5OH^- \xrightarrow{\text{controlled pH}} La(OH)_3 + Co(OH)_2 + 5NO_3^- \quad \ldots(14)$$

Calculation of pH for coprecipitation of $La(NO_3)_3$ and $Co(NO_3)_3$ (Srichaisiriwech, 2002)

Coprecipitation of $La(OH)_3$ and $Co(OH)_2$ for the preparation of $LaCoO_3$ can be done by controlling pH of the solution which was calculated from K_{sp} of each salt.

$La(NO_3)_3$ and $Co(NO_3)_2$ 0.2000 M 25.00 cm^3 each.

K_{sp} of $La(NO_3)_3 = 2.0 \text{ x } 10^{-19}$

Total volume after combining the two solutions is 50.00 cm^3

The concentration of La^{3+} in 50.00 cm^3 is $= \dfrac{0.2000\,\text{mol}}{1000\,\text{cm}^3} \times \dfrac{25.00\,\text{cm}^3}{50.00\,\text{cm}^3} \times 1000\,\text{cm}^3$

$$= 0.1000 \text{ M}$$

$$[La^{3+}]\,[OH^-]^3 = K_{sp}$$

$$[OH^-] = 3\sqrt{\frac{2.0 \times 10^{-19}}{0.1000}}$$

$$[OH^-] = 1.3 \text{ x } 10^{-6} \text{ M}$$

$$pOH = 5.9$$

$$pH = 8.1$$

K_{sp} of $Co(NO_3)_2 = 1.0 \text{ x } 10^{-15}$

The concentration of Co^{2+} in 50.00 cm^3 is $= \dfrac{0.2000\,\text{mol}}{1000\,\text{cm}^3} \times \dfrac{25.00\,\text{cm}^3}{50.00\,\text{cm}^3} \times 1000\,\text{cm}^3$

$$= 0.1000 \text{ M}$$

$$[Co^{2+}]\,[OH^-]^2 = K_{sp}$$

$$[OH^-] = 2\sqrt{\frac{1.0 \times 10^{-15}}{0.1000}}$$

$$[OH^-] = 1.0 \text{ x } 10^{-7} \text{ M}$$

$$pOH = 7.0$$

$$pH = 7.0$$

Therefore, pH > 8.1 is needed to initiate the coprecipitation of $La(OH)_3$ and $Co(OH)_2$. The concentration of each solution is calculated from each pH value as follows:

at pH 9;

$$[La^{3+}]\,[OH^-]^3 = 2.0 \text{ x } 10^{-19}$$

$$[La^{3+}] = \frac{2.0 \times 10^{-19}}{\left(1 \times 10^{-5}\right)^3}$$

$$[La^{3+}] = 2.0 \times 10^{-4}\ M$$

$$[Co^{2+}]\,[OH^{-}]^2 = 1.0 \times 10^{-15}$$

$$[Co^{2+}] = \frac{1.0\times10^{-15}}{\left(1\times10^{-5}\right)^2}$$

$$[Co^{2+}] = 1.0 \times 10^{-5}\ M$$

At pH 9, the concentrations of La^{3+} and Co^{2+} are 2.0 x 10^{-4} and 1.0 x 10^{-5} M, respectively. In Figure 25, the calculated concentrations plotted as a function of pH are shown. The concentration of La^{3+} and the concentration of Co^{2+} at pH 10.3 are precipitated in approximate ratio of 1:1.

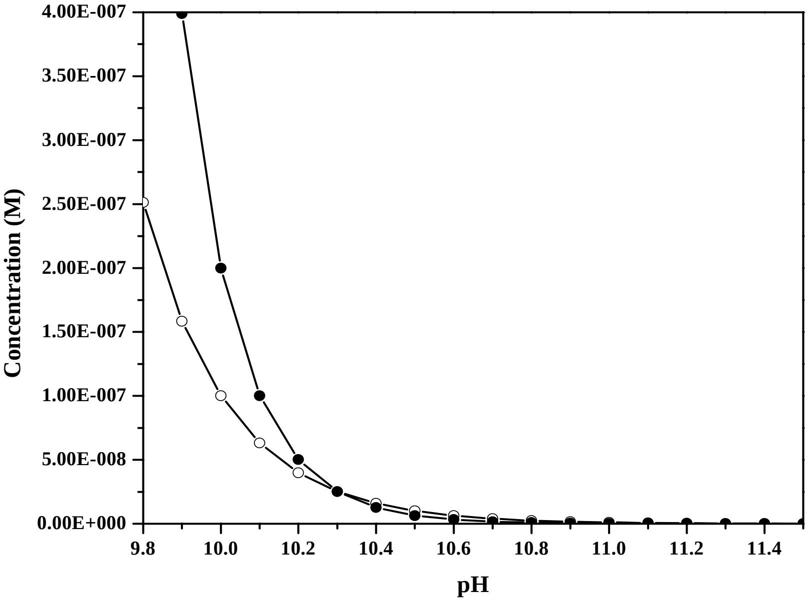


Figure 25 pH effect on precipitation of $La(OH)_3$ and $Co(OH)_2$ (● = $[La^{3+}]$ and ○ = $[Co]^{2+}$)

Source: Srichaisiriwech (2002)

Srichaisiriwech (2002) prepared $LaCoO_3$ by the coprecipitation method using $La(OH)_3$ and $Co(OH)_2$ at pH 8.52 - 10.95 of which the XRD results are shown in Figure 26. The coprecipitates at pH 9.25 showed high crystallinity with a little amount of impurity. Therefore, pH 9.25 was used for the coprecipitation of $La(OH)_3$ and $Co(OH)_2$ to form perovskite $LaCoO_3$ through out this experiment.

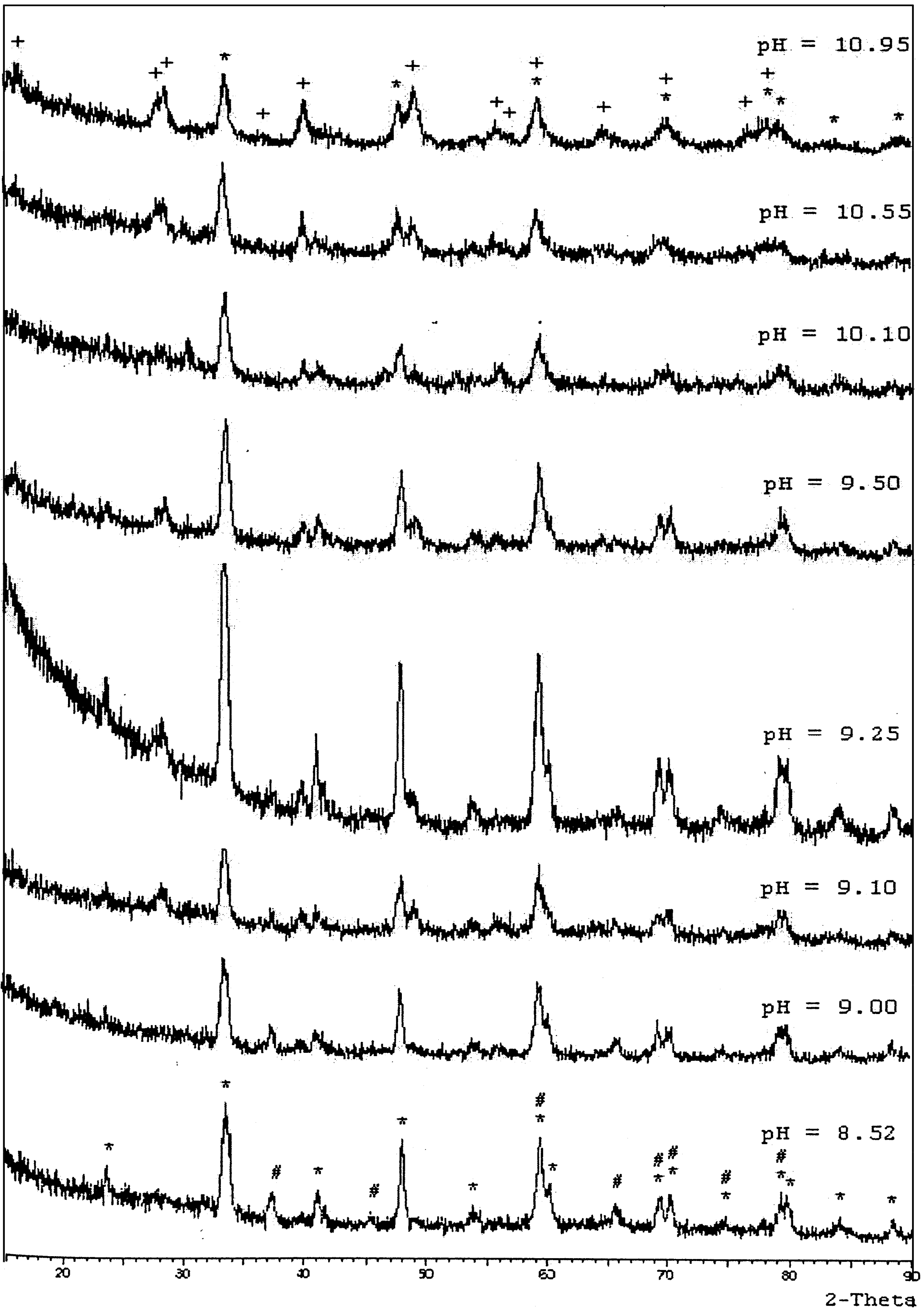


Figure 26 X-ray diffraction patterns of $LaCoO_3$ at different pH (* = $LaCoO_3$, + = $La(OH)_3$ and # = Co_3O_4)

Source: Srichaisiriwech (2002)

1.3.1 Preparation of coprecipitates $La(OH)_3$ and $Co(OH)_2$

Solutions of $La(NO_3)_3$ in distilled water 0.2000 M 25.00 cm^3 and $Co(NO_3)_2$ in distilled water 0.2000 M 25.00 cm^3 were mixed and 5% NH_4OH as a precipitating agent was slowly added into the stirring mixture until pH 9.2 was reached (Srichaisiriwech, 2002). $La(OH)_3$ and $Co(OH)_2$ precipitates were formed. They were filtered off and dried at 383 K for 3 h. During calcinations, the hydroxide precipitates were transformed to the perovskite-type oxide.

Heating steps for calcination of the dried sample were set as follows:

- The first step: the temperature was increased from room temperature to 473 K and held for 2 hours with flowing N_2 of 50 cm^3min^{-1},
- The second step: the temperature was raised to 623 K with flowing N_2 of 70 cm^3min^{-1} and O_2 of 30 cm^3min^{-1}.
- The last step: the temperature was heated up to 973 K with flowing N_2 and O_2 of 50 cm^3min^{-1} each. A ramp rate of all processes was 1.7 $Kmin^{-1}$.

Preparations of $LaCoO_3$ for FTIR study were the same as that described above with the exception that the calcination temperatures were step up to 973 K.

Preparations of $LaCoO_3$ for XRD were the same as that described above with the exception the samples were calcined at 773, 823, 873 and 973 K. Sample codes of the catalysts prepared by coprecipitation according to the heating conditions were assigned as shown in Table 7.

Table 7 Sample codes of the catalysts prepared by coprecipitation according to heating conditions

Sample	Heating temperature (K)	Hold up time (h)	Sample code
CP	383	12	CP383-12
La-CP	383	12	La-CP383-12
Co-CP	383	12	Co-CP383-12
LC-CP	383	12	LC-CP383-12
LC-CP	423	3	LC-CP423-03
LC-CP	473	3	LC-CP473-03
LC-CP	523	3	LC-CP523-03
LC-CP	573	3	LC-CP573-03
LC-CP	623	3	LC-CP623-03
LC-CP	773	3	LC-CP773-03
LC-CP	773	8	LC-CP773-08
LC-CP	823	3	LC-CP823-03
LC-CP	873	3	LC-CP873-03
LC-CP	973	8	LC-CP973-08

2. Catalyst Characterization

$LaCoO_3$ catalysts have been characterized. Thermal decomposition behaviors were studied by thermogravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR). Crystallinity and crystallite size analysis were performed using powder x-ray diffraction (XRD). Elemental analysis was obtained by x-ray fluorescence spectroscopy (XRF). Oxidation states of the samples were investigated using x-ray photoemission spectroscopy (XPS). BET surface areas of the prepared catalysts have been measured by nitrogen adsorption.

2.1 Thermogravimetric analysis (TGA)

Thermal decomposition behaviors of the as-prepared samples were studied by a TGA 7 Perkin Elmer analyzer. The as-prepared gels (or precipitates) were carried out in nitrogen gas, with a heating rate of 3.4 $\mathrm{Kmin^{-1}}$. Studied temperature range was 303 to 973 K. α-Al_2O_3 was used as the reference material.

2.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the as-prepared gels and the calcined samples from both sol-gel methods were obtained from a system 2000 FTIR Perkin Elmer spectrometer, equipped with a DTGS detector. Spectra were collected with a resolution of 4 cm^{-1} using 32 scans in the range 4000-400 cm^{-1}. All samples were prepared using KBr pellet.

2.3 Powder x-ray diffraction (XRD)

2.3.1 Determination of crystallinity

All calcined samples were analyzed by powder x-ray diffraction (XRD). The XRD experiments were performed on a Phillips X' pert x-ray diffractometer using Cu K_α radiation (λ = 1.54 Å) and a curved graphite monochromator. The x-ray source was operated at 40 kV and 30 mA. The powder x-ray diffractograms were recorded at step size 0.01^{o} with 0.5 count s^{-1} accumulation per step. Data were collected between 2θ: 10 to 90 degree. The diffraction patterns have been indexed by comparison with the JCPDS files (Joint Committee on Powder Diffraction Standards).

2.3.2 Determination of crystallite size

Crystallite size (D) is determined from XRD pattern using the Scherrer equation (equation 10) (Klung and Alexander, 1954).

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is a constant equal to 0.90 (Bergeret and Gallezot, 1997), λ is the incident x-ray wavelength, λ_{Cu} equal to 1.54 Å, θ is the diffraction angle in degrees and β is the peak breadth in radians. The true peak breadth is calculated by the Warren formula (equation 11)

$$\beta^2 = \beta^2_{\text{observed}} - \beta^2_{\text{reference}}$$

where β_{observe} is the full width at half maximum intensity (FWHM) of measured sample peak in radians. $B_{\text{reference}}$ is the full width at half maximum intensity (FWHM) of standard peak or instrument broadening in radians, which is obtained from diffraction pattern of standard. The instrument broadening ($\beta_{\text{reference}}$) was obtained using α-Al_2O_3 as the standard material, which was prepared by calcination of Al_2O_3 at 1573 K for 4 hours under normal atmospheric pressure. The structure of α-Al_2O_3 was characterized by an x-ray diffractometer and compared with JCPDS 83-2081 (α-Al_2O_3).

Experimental

Experimental steps for crystallite size determination were followings:

- First, determining line broadening due to the x-ray diffractometer used.

Observed XRD peaks of α-Al_2O_3 (2θ was 25.51, 35.09, 37.71, 43.30, 52.50 and 57.45 degree) (Figure 27) were expanded to determine full width at half maximum intensity (FWHM), summarized in Table 4.

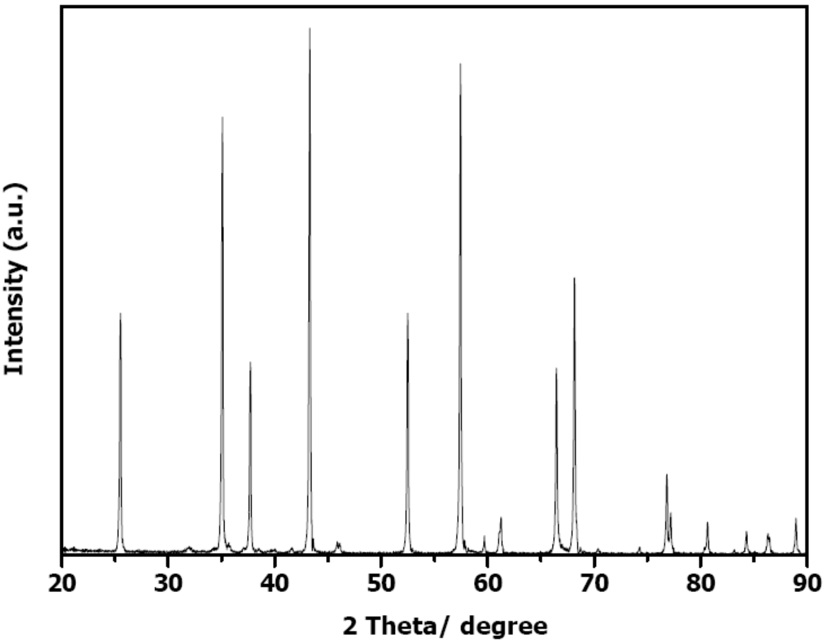


Figure 27 X-ray diffraction patterns of α-Al_2O_3 calcined at 1573 K

Table 8 Instrument broadening (FWHM, $\beta_{reference}$)

2Theta	FWHM $\beta_{reference}$ (2Theta)	FWHM $\beta_{reference}$ (rad.)
25.51	0.154	0.00269
35.09	0.154	0.00269
37.71	0.151	0.00264
43.30	0.151	0.00264
52.50	0.150	0.00262
57.45	0.151	0.00264

Plotted FWHM as a function of diffraction angles and used as a calibration curve for determination of instrument line-broadening ($\beta_{reference}$) as shown in Figure 28. The value of $\beta_{reference}$ is given by equation 15.

$$\beta_{reference} = 0.0027\ e^{-0.008 \times 2\theta} \qquad \text{.....(15)}$$

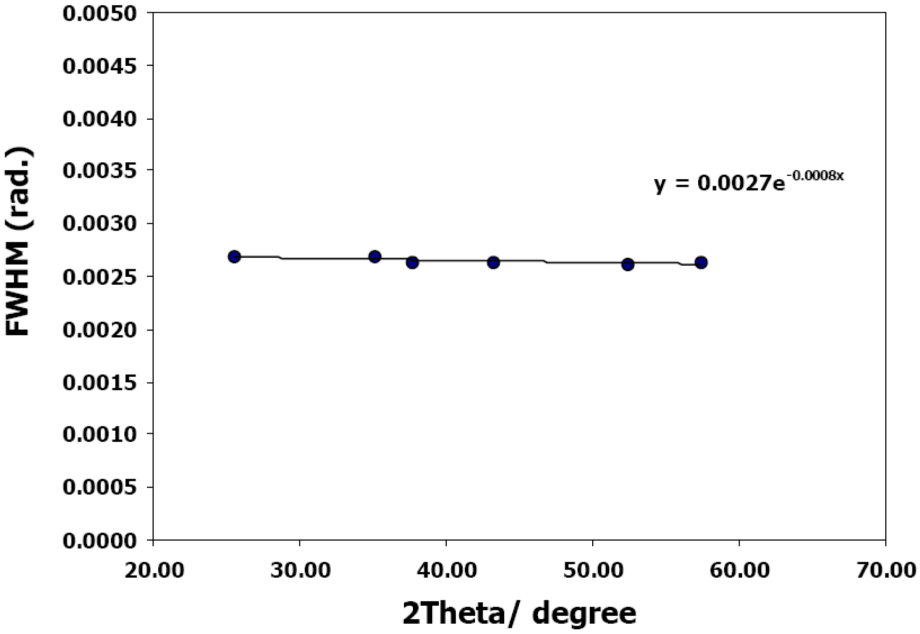


Figure 28 Calibration curve for determination of instrument broadening ($\beta_{reference}$)

- Second, determining the full width at half maximum intensity (FWHM-$\beta_{observe}$) of samples by expansion the diffraction peak corresponding to the (0 2 4) plane of perovskite phase.
- Third, calculating the instrument line broadening of each sample using the calibration curve and calculating the true peak breadth using the Warren formula (equation 11).
- Finally, calculating the crystallite size of the samples using the Scherrer equation (equation 10).

2.4 X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out at the Siam Photon Laboratory using a VG Scientific concentric hemispherical analyzer. Powder samples were pressed on carbon tape mounted on a molybdenum plate. The excitation scan was 400 watt Al K_{α} (1486.68 eV) and the pass energy of the analyzer was 50 eV. All binding energies were referred to the C 1s line at 285.0 eV and Au $4f_{7/2}$ line at 83.5 eV.

The prepared samples on the molybdenum plate placed on a holder in vacuum system at 10^{-4} torr using a rotary pump and a turbo pump and then decreased pressure in the system to 10^{-8} torr using an ion pump. Finally, the sample holder was transferred to the analysis chamber.

The energy scanning range depends on each element as shown in Table 9. Data analysis involving curve fitting, integration, area measurement, and peak marking was performed on the Avantage program.

Table 9 The energy scanning ranges (eV), energy step and number of scan of the investigated elements

Elements	Start (eV)	End (eV)	Step (eV)	No. of scan
C	275	295	0.1	10
O	500	560	0.1	10
La	800	885	0.1	10
Co	750	820	0.1	10

2.5 X-ray fluorescence spectroscopy (XRF)

Percentage weight of catalyst compositions were determined quantitatively using XRF spectroscopic method. Sample powder was ground by ball-mill to stuff as a pellet. The patterns were collected on a Phillips PW 2400 spectrometer using the wavelength dispersive system. LiF (220), crystal 2d = 0.2848 nm with duplex mounted sealed Xe gas detector was used for La element. LiF (200), crystal 2d = 0.4027 nm with flow detector was used for Co elements. The results were recorded in percentage weight, according to the reference material standards of the SemIQ analytic program. The calibrations of the measurements were carried out by the external standard method.

2.6 Nitrogen adsorption isotherm

Surface areas of the samples were determined by N_2 adsorption isotherms, evaluated from the BET equation. The experiment was performed on a micromeritics Chemisorb 2750 instrument. Prior to each measurement, the sample was degassed for 1 hour at 473 K under nitrogen gas with flow rate 15 cm^3min^{-1}. The sample cell was immersed into liquid nitrogen. 30% Nitrogen/Helium gas was admitted with flow rate 15 cm^3min^{-1}. The surface area was determined by the BET equation.

3. Catalytic Oxidation of Toluene

Toluene was used as a representative substance to study the catalytic activity of prepared catalysts for oxidation reaction. The activity of each catalyst was determined in terms of absorbance intensity ratio at 2920 cm^{-1}, which is the absorbed frequency due to C–H stretching of methyl group, of the unconverted toluene relative to the starting toluene as a function of time. The catalytic oxidation process was carried out in an environmental chamber and reaction products were analyzed *in situ* by DRIFTS.

3.1 Apparatus

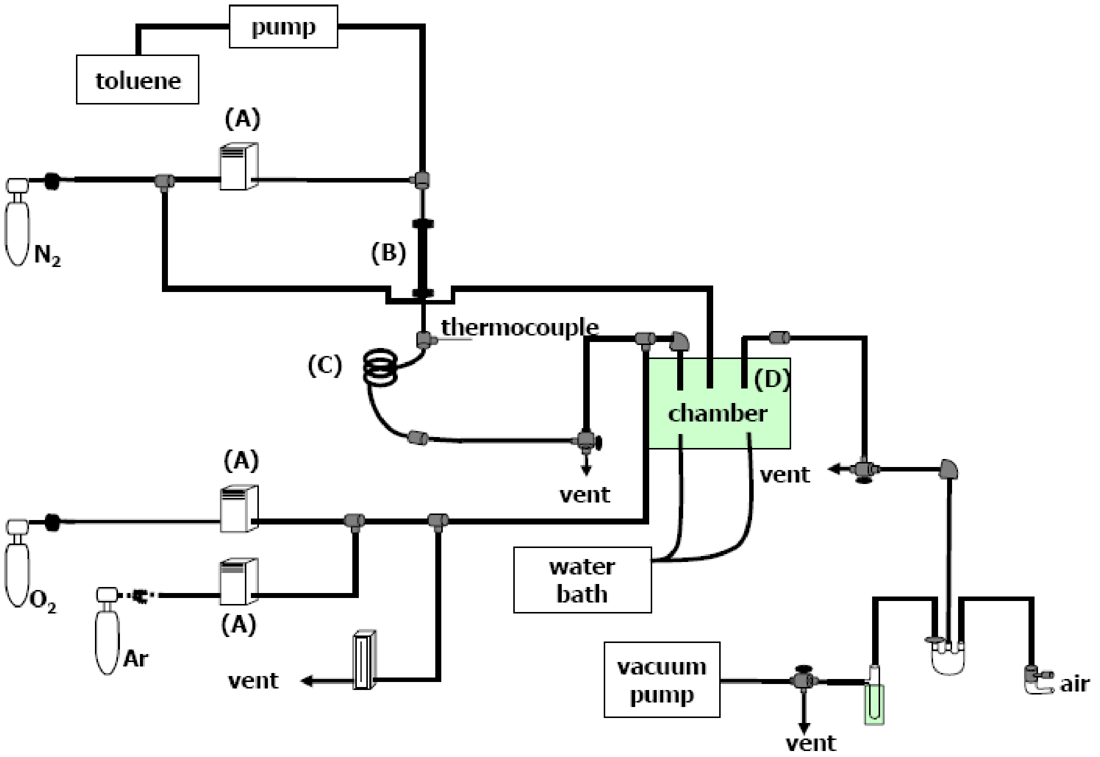


Figure 29 Schematic of the system set up for catalytic activity testing: (A) mass flow controller, (B) vaporizer, (C) mixing coil and (D) DRIFT spectrometer

The apparatus flow chart presented in Figure 29 is separated into three paths, namely: gas system, a vaporizer and analytical system.

a) Gas system

Nitrogen, air, and argon used via gas system were equipped with 316-stainless steel tube (1/8-inch in diameter), ball valves, and mass flow controller (A). Nitrogen connected to vaporizer (B) is used as carrier gas for mixing with toluene in the vaporizer and throughout the system. O_2 mixed with Ar, which are connected to the outlet of the vaporizer, are used as the oxygen source for catalyst pretreatment and catalytic oxidation. All gases are introduced through a stainless steel tube and regulated by a mass flow controller. A ball valves equipped with a mass flow controller is used as a switch prior through the flowing system.

b) A vaporizer

A vaporizer (B) used to vaporize liquid toluene by thermal treatment at 423 K, made from a 316-stainless steel tube, 3/8 inch in diameter and 20 cm long packed with metal gauze (Figure 30). Thermocouple is set at the outlet of the vaporizer to measure the temperature of the vaporized toluene. The radial mixing between vapor phase sample and carrier gas is carried out in a coil tube (C), setting at the outlet position.

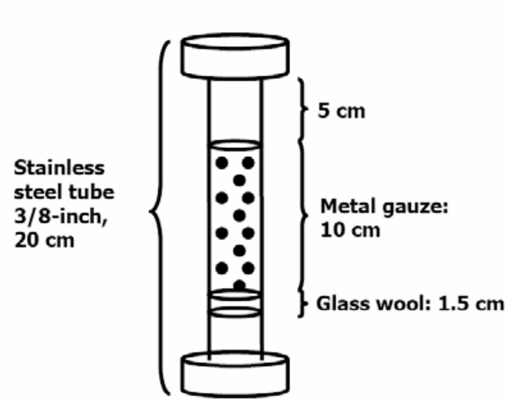
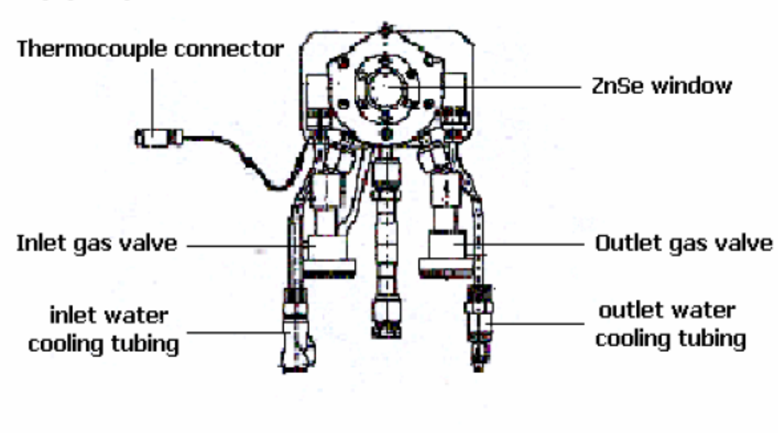


Figure 30 Cross-section of the vaporizer (B) in the Schematic of the system set up for catalytic activity testing

c) Analytical system

The analytical system, locating in DRIFTS chamber (Figure 29-D), consists of an environmental chamber, a temperature controller and reflectance accessory. The environmental chamber (Figure 31) is constructed from 316-stainless steel. The standard chamber window is ZnSe, which has cut-off at 650 cm^{-1}. Temperature within the chamber is controlled by Specac 3000 Series Temperature Controller. The selector diffuse reflectance accessory is an important part for DRIFTS. The selector has 2 ellipsoidal mirrors, 2 input mirrors and 2 output mirrors. These are used to focus infrared radiation from source to the sample and to collect the diffusing light to the detector made of Mercury Cadmium Telluride (MCT).

(a) Top view



(b) Side view

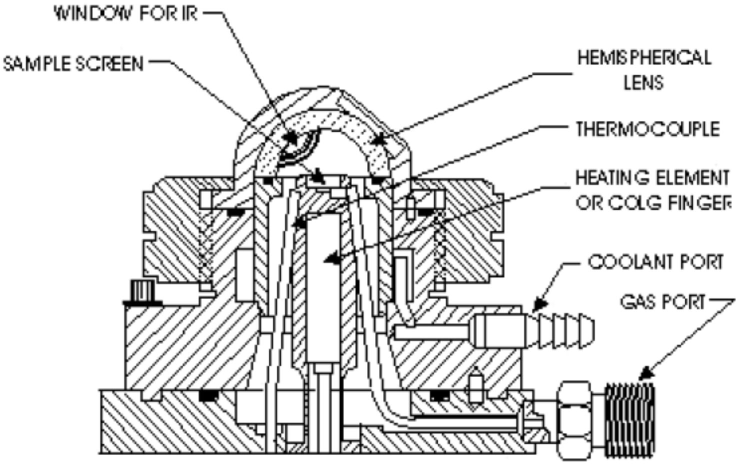


Figure 31 An environmental chamber

(a) Top view

(b) Side view

Due to the normal phase of toluene being liquid, stainless steel tube connecting to the environmental chamber must be heated at 423 K by heating tape and temperature controller to present condensation.

3.2 Procedure

3.2.1 Catalyst pretreatment

The catalyst was placed into a sample holder which is under ZnSe window in the environmental chamber and evacuated at room temperature for 1 hour, then heated the catalyst up to 723 K. Ar/O_2-mixed gases (50/50) with flow rate 23.7 cm^3min^{-1} was introduced into the environmental chamber to oxidize the catalyst before adsorption process.

3.2.2 Adsorption process

According to the flow chart of the apparatus presented in Figure 29, toluene was fed into the vaporizer (B), where it was mixed with the carrier gas (N_2), using a Masterflex pump with flow rate 0.6033 cm^3min^{-1}. In order to achieve a constant toluene evaporation rate, the temperature in the vaporizer was controlled at 423 K. The toluene vapor mixed with N_2 was introduced to the environmental chamber with the flow rate 12.50 cm^3min^{-1} for 15 minutes and then the inlet and outlet gas valves of environmental chamber were closed for 30 minutes allowing adsorption of toluene on the catalyst surface to occur.

3.2.3 Oxidation process

Before the reaction was started, Ar was passed the surface of the catalyst for 2 hours to remove gaseous toluene over the surface and there was only adsorbed toluene on the catalyst surface. Then gaseous mixture of Ar and O_2 (50/50) with the flow rate 23.7 cm^3min^{-1} was introduced into the environmental chamber of which temperature was 723 K and the reaction was started.

DFIRTS spectra were recorded in every minute of the experimental using OPUS program.

Table 10 Reaction conditions for the catalytic oxidation of toluene on $LaCoO_3$ catalysts

Reaction Conditions	
Temperature, K	393 or 423
Pressure, kPa	180
Feed of toluene, mmol s^{-1}	0.004
Feed of oxygen, mmol s^{-1}	0.006