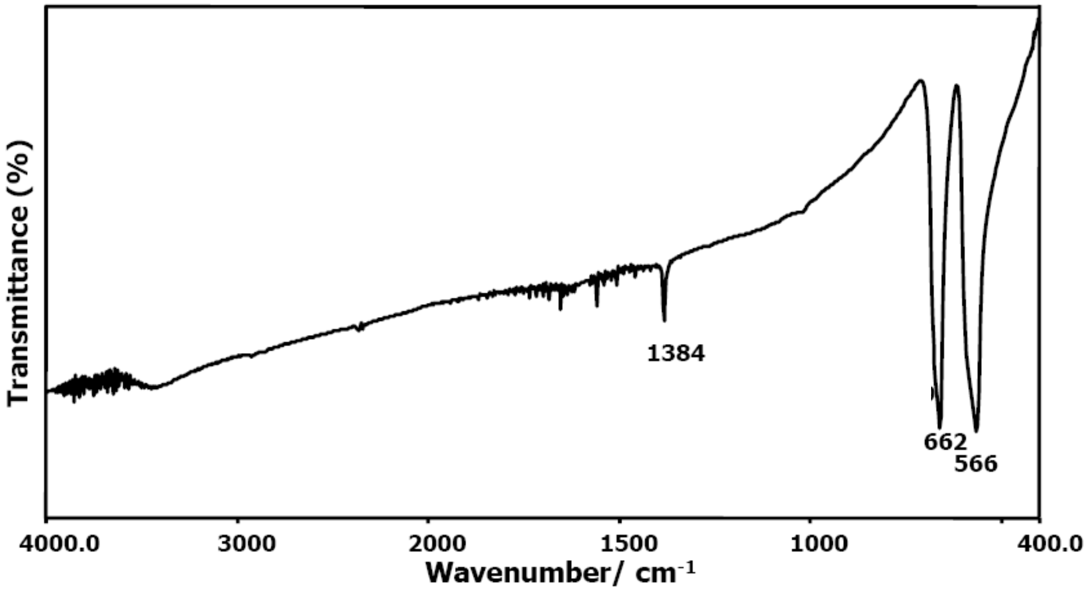
APPENDIX

APPENDIX A

FTIR spectroscopy was performed to information of the structure and composition of $Co(NO)_3 \cdot 6H_2O$ calcined at 773 K for 3 hours.



Appendix Figure A1 FTIR spectrum of $Co(NO)_3 \cdot 6H_2O$ calcined at 773 K

In Figure A1 showed the bands at 662 and 566 cm^{-1} which corresponded to the Co–O bond stretching in Co_3O_4 (638 and 542 cm^{-1}, Jiu *et al.*, 2002). The absorption band at 1384 cm^{-1} was attributed to nitrate (Sinquin *et al.*, 2001).

Appendix Table A1 FTIR spectra assignment of $Co(NO)_3 \cdot 6H_2O$ calcined at 773 K

Functional group / Catalysts	Wavenumber (cm^{-1})	
	N–O bending of nitrate ion	Co–O stretching
Reference	1384[(a)]	638, 542[(b)]
$Co(NO)_3$-773-03	1384	662, 566

[(a)] Sinquin *et al.* (2001) [(b)] Jiu *et al.* (2002)

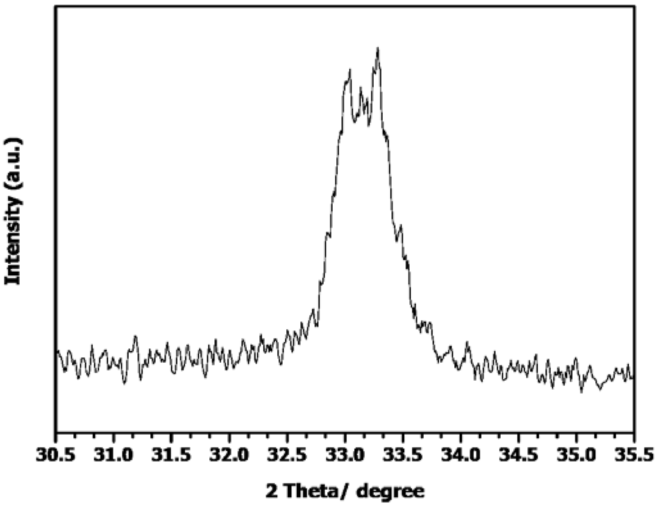
The XRD reference patterns of JCPDS files

Appendix Table A2 The JCPDS file of $LaCoO_3$ with the number: 25-1060

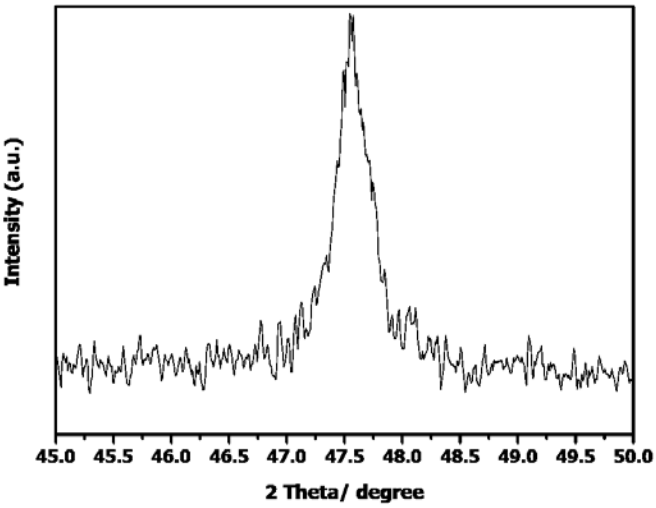
2 Theta (degree)	d-spacing (Å)	Relative Intensity (%)	Miller Indices		
			h	k	l
23.266	3.820	20	0	1	2
32.914	2.719	100	1	1	0
33.304	2.688	95	1	0	4
38.992	2.308	2	1	1	3
40.662	2.217	25	2	0	2
41.344	2.182	8	0	0	6
47.515	1.912	70	0	2	4
53.277	1.718	10	1	2	2
53.818	1.702	8	1	1	6
58.722	1.571	35	3	0	0
59.011	1.564	55	2	1	4
59.767	1.546	20	0	1	8
68.974	1.360	20	2	2	0
69.943	1.344	25	2	0	8
73.887	1.282	4	3	1	2
74.361	1.275	6	3	0	6
75.302	1.261	2	1	0	10
78.789	1.214	20	1	3	4
79.462	1.205	20	1	2	8
83.269	1.159	4	0	4	2
83.711	1.154	8	2	2	6

The determination of the full width at half maximum intensity ($\beta_{observed}$)

In generally, the $\beta_{observed}$ used in the Warren formula is usually obtained from diffraction pattern of the full width at half maximum intensity (FWHM) of measured sample peak. The highest intensity of the XRD peak of prepared $LaCoO_3$ was expanded to determine the FWHM. In Figure A2 shows peak spliting at 30.0° (d_{110}) and 33.3° (d_{104}), thus the FWHM obtained from this position might result some error. Instead, the second highest intensity of the XRD peaks of prepared $LaCoO_3$ (d_{024}) was chosen to determine the FWHM (Figure A3) and was expanded to determine the $\beta_{observed}$ for use in Warren formula.



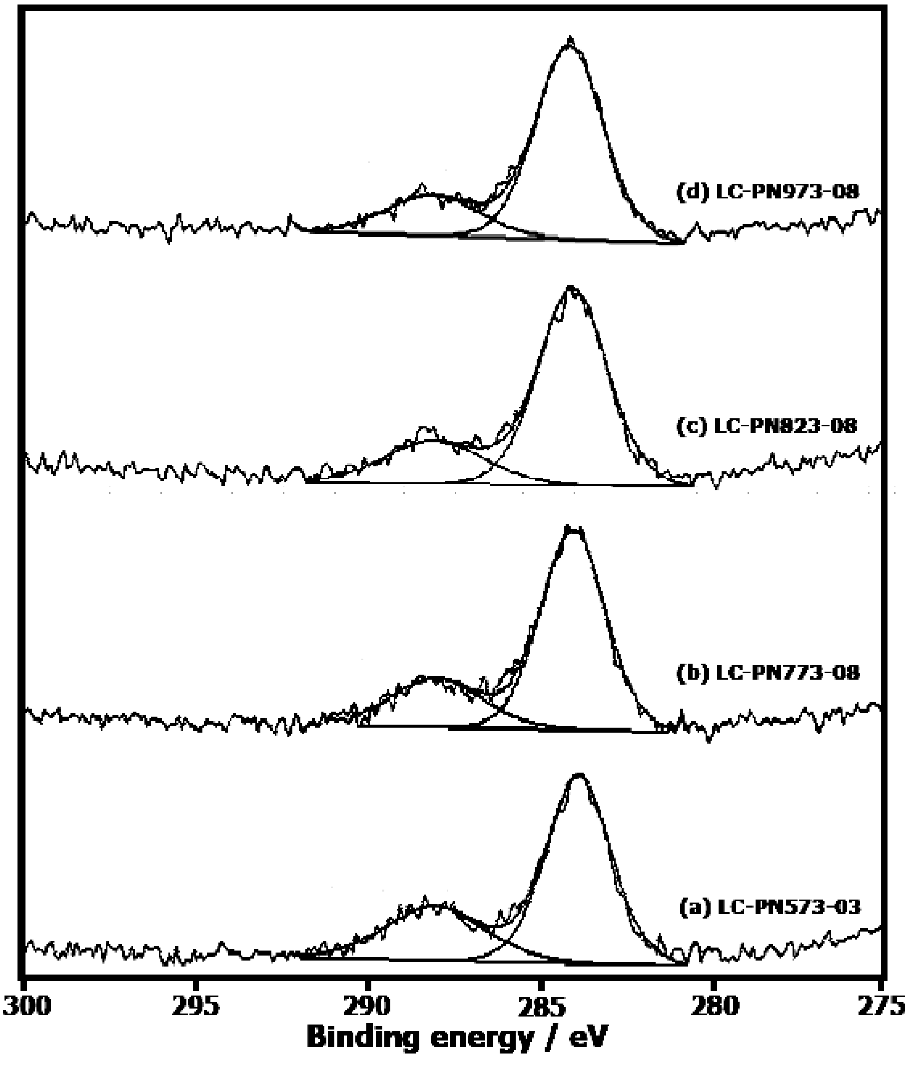
Appendix Figure A2 X-ray diffraction pattern of expansion of peak at d_{110}



Appendix Figure A3 X-ray diffraction pattern of expansion of peak at d_{024}

APPENDIX B

The C 1s photoelectron spectra of $LaCoO_3$ prepared by the Pechini, Schiff base complex and the coprecipitation methods are presented in Figures B1 – B3 and the resulting binding energy values were corrected using C 1s peak at 285 eV are listed in Tables B1 – B3.



Appendix Figure B1 C 1s photoelectron spectra of the samples prepared by the Pechini method

C 1s Binding energy of LC-PN973-08 at 284.1 eV.

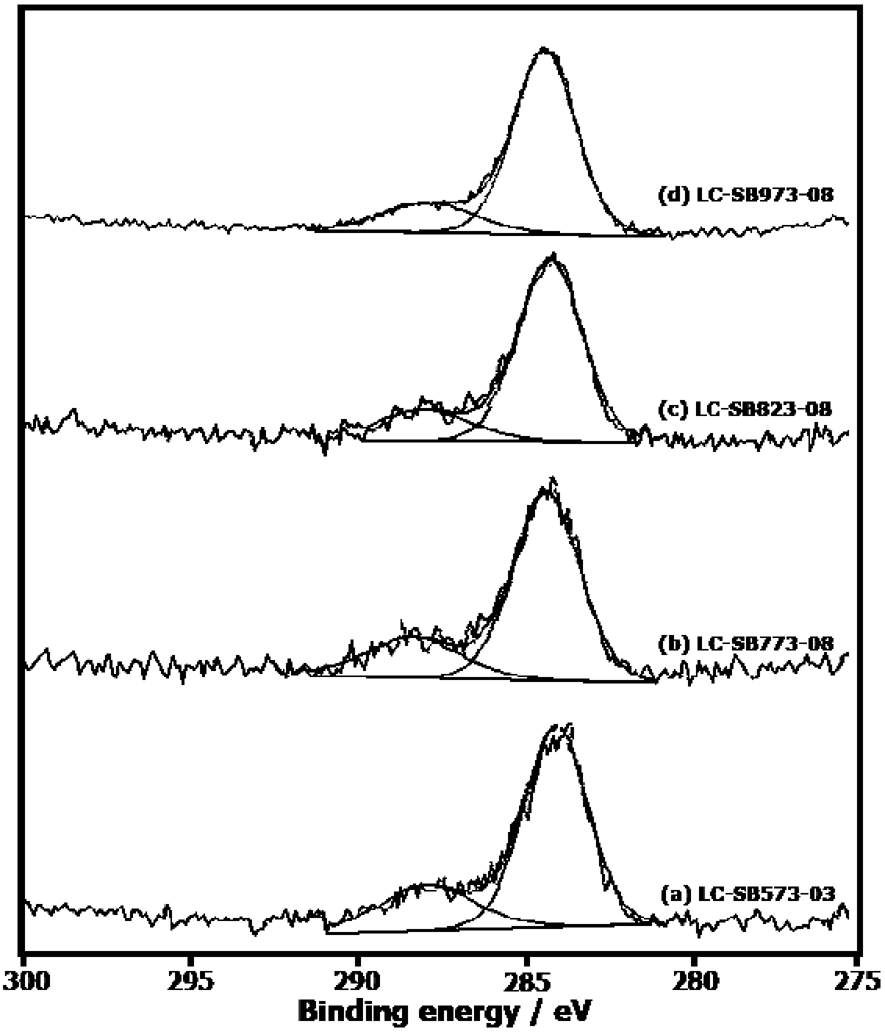
C 1s Binding energy of LC-PN823-08 at 284.1 eV.

C 1s Binding energy of LC-PN773-08 at 284.0 eV.

C 1s Binding energy of LC-PN573-03 at 284.0 eV.

Appendix Table B1 Binding energies of C 1s for $LaCoO_3$ prepared by the Pechini method

Catalyst	C 1s	
	Binding energy (eV)	Area
LC-PN573-03	285.0	2852.84
	289.2	1223.98
LC-PN773-08	285.0	2978.87
	289.0	1028.11
LC-PN823-08	285.0	3190.19
	289.0	990.12
LC-PN973-08	285.0	2948.80
	288.9	853.30



Appendix Figure B2 C 1s photoelectron spectra of the samples prepared by Schiff base complex method

C 1s Binding energy of LC-SB973-08 at 284.3 eV.

C 1s Binding energy of LC-SB823-08 at 284.2 eV.

C 1s Binding energy of LC-SB773-08 at 284.2 eV.

C 1s Binding energy of LC-SB573-03 at 284.1 eV.

Appendix Table B2 Binding energies of C 1s for $LaCoO_3$ prepared by the Schiff base complex method

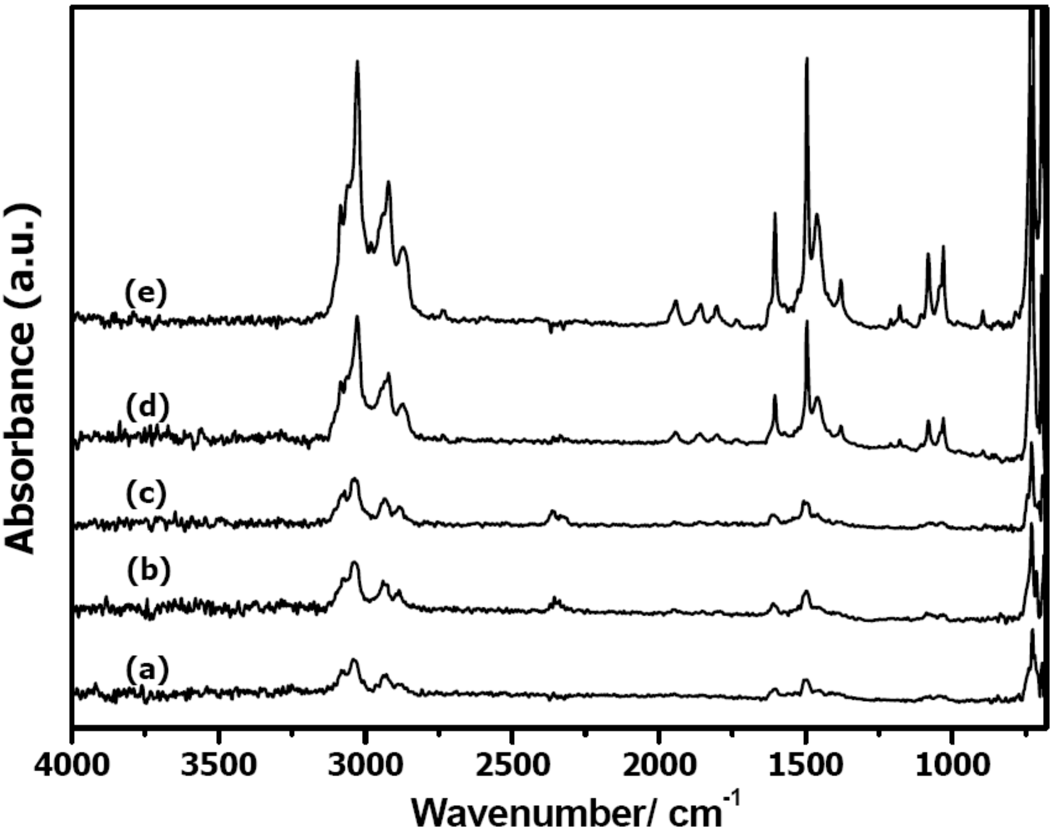
Catalyst	C 1s	
	Binding energy (eV)	Area
LC-SB573-03	285.0	5622.37
	288.8	1913.83
LC-SB773-08	285.0	5011.04
	289.0	1562.90
LC-SB823-08	285.0	5865.81
	288.9	1472.17
LC-SB973-08	285.0	5563.68
	288.5	1339.81

APPENDIX C

Optimization of flow rate of toluene

Appendix Table C1 The flow rate of toluene at various pump drive speeds

Speed of toluene (rpm)	Flow rate of toluene ($cm^3 min^{-1}$)
50	0.1274
70	0.2637
80	0.3290
90	0.3979
100	0.4631



Appendix Figure C1 DRIFTS spectra of flow rate comparison of toluene at (a) 50, (b) 70, (c) 80, (d) 90 and (d) 100 rpm adsorbed on LC-SB-773

The comparison flow rate of adsorbed toluene is showed in Figure C1 and the data corresponding to flow rate are summarized in Table C1. The highest flow rate was showed high absorbance intensity. The optimized flow rate was 90 rpm (0.3979 cm^3). The adsorption of toluene on catalyst was over absorbance intensity when using the flow rate higher than 90 rpm when using flow rate at 100 rpm. Therefore, the flow rate used for feeding toluene to environmental chamber is 0.3979 cm^3.

APPENDIX D

PRESENTATION

Preparation of nano-$LaCoO_3$ perovskite by sol-gel methods:
the Pechini and Schiff base complex

Praewpilin Kangvansura and Attera Worayingyong

The abstract of 32nd Congress on Science and Technology of Thailand (STT 2006),
Queen Sirikit National Convention Center (QSNCC), Bangkok, Thailand,
10-12 October 2004.

การเตรียมสารประกอบเพอรอฟสไกท์นาโนแลนทานัมโคบอลต์ออกไซด์โดยวิธีโซล-เจล: เพคินีและสารเชิงซ้อนชิฟเบส

Preparation of nano-$LaCoO_3$ perovskite by sol-gel methods: the Pechini and Schiff base complex

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บทคัดย่อ: นาโนแลนทานัมโคบอลต์ออกไซด์เตรียมโดยวิธีโซลเจลโดยใช้สารเชิงซ้อนของเพคินีและชิฟเบส วิเคราะห์คุณลักษณะด้วยเทคนิค Fourier transform infrared spectroscopy (FTIR) และ x-ray diffraction (XRD) พบว่า $LaCoO_3$ที่เผาที่อุณหภูมิ 500 องศาเซลเซียส เป็นโมโนเฟสและมีขนาดผลึก 12-13 นาโนเมตร IR สเปกตราพบพันธะ Co–O บ่งบอกได้ว่าเป็นโครงสร้างของ $LaCoO_3$ และการศึกษากัมมันตภาพของ $LaCoO_3$ ที่เป็นตัวเร่งในปฏิกิริยาออกซิเดชันของโทลูอีนโดยเทคนิค diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) พบว่า $LaCoO_3$ ที่มีขนาดเล็กโดยไม่มีสิ่งปนเปื้อนเป็นตัวเร่งปฏิกิริยาที่ดีที่สุด $LaCoO_3$ เตรียมโดยวิธีโซลเจลโดยใช้สารเชิงซ้อนของชิฟเบสมีกัมมันตภาพในการเร่งปฏิกิริยาสูงกว่าการเตรียมด้วยเพคินี

Abstract: Nano-$LaCoO_3$ was prepared by sol-gel method using the Pechini (PC) and Schiff base (SB) complex. The resulting powders were characterized by fourier transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD). The formation of monophase $LaCoO_3$ and the crystallite sizes of 12-13 nm took place upon calcination at 773 K for 8 hours. IR spectroscopy revealed the presence of Co–O bond typical of $LaCoO_3$ structure. DRIFTS study of the toluene oxidation on PC and SB-$LaCoO_3$ showed that the small-sized perovskites without impurity performed the best. $LaCoO_3$ prepared by sol-gel method using the Schiff base complex performed higher catalytic activity than that prepared by the Pechini.

Introduction: Perovskites, with the general structural formula ABO_3, are the interesting mixed oxides that have widely been studied due to their activities in the oxidation of carbon monoxide, methane, hydrocarbons. Perovskites can be produced by using polymerizable complex process, which allows reproducibility and homogeneity. In the present work, two approaches of the sol-gel methods; the Pechini and Schiff base complex, have been proposed in order to achieve the highly homogeneous $LaCoO_3$. The effect of the preparation procedure and the calcination temperature on the formation of $LaCoO_3$ was investigated. Infrared spectroscopy was used to analyze the thermal decomposition behaviors and x-ray diffraction was used to characterize the perovskite structure and crystallite size. The catalytic activity of $LaCoO_3$ was tested using toluene oxidation as a model and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) was used to investigate *in situ* reactions on the catalyst surface through monitoring spectral features of the adsorbed molecules.

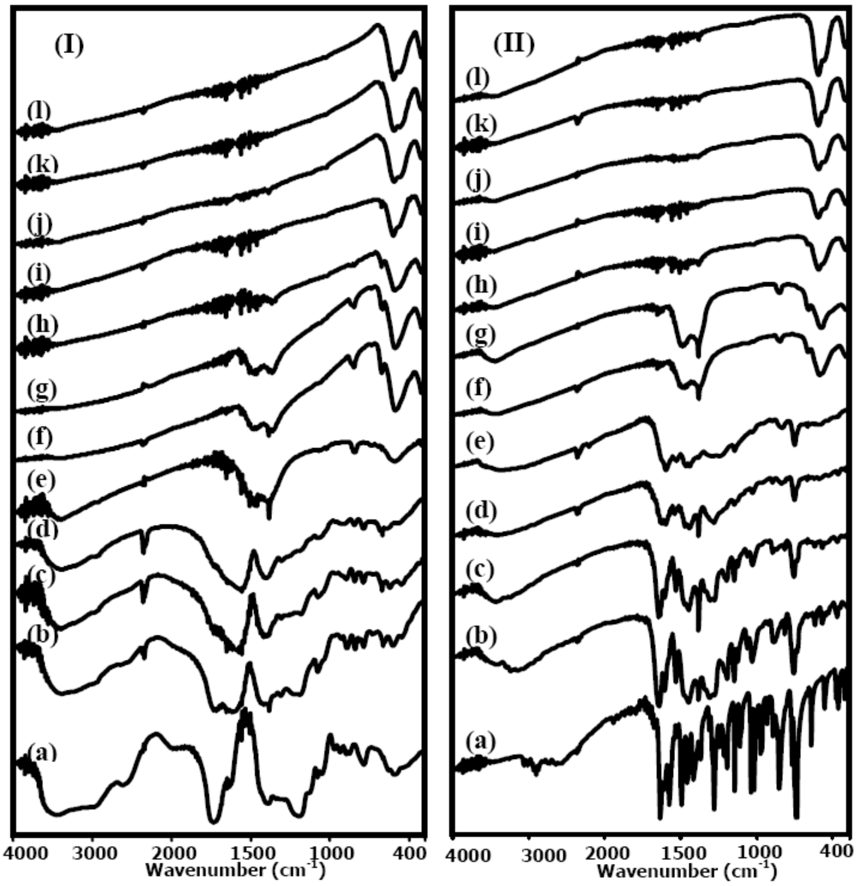
Methodology: Gels for $LaCoO_3$ perovskite were prepared by sol-gel method with two approaches as follows: (i) the Pechini method (PC): $La(NO_3)_3$ and $Co(NO_3)_2$ were the precursors with citric acid using as complexing agents and ethylene glycol using for polymerization of the complexes at 363 K for 3 h. The resulting resin was dried at 383 K to form as-prepared gel (LCO-PC). (ii) The Schiff base method (SB): $La(NO_3)_3$ and $Co(NO_3)_2$ were also the precursors. Before the complexation was started, salicylaldehyde and ethylene diamine were mixed and stirred in order to obtain the Schiff base ligand at 328 K for complexation of La^{3+} and Co^{2+} ions. After drying at 383 K, the as-prepared gel (LCO-SB) was formed. Samples for the measurements of IR spectra and XRD patterns were prepared by calcination of the precursors for 3 or 8 h at desired temperatures under flowing O_2 and N_2 with the ratio of 50:50. Toluene adsorption and oxidation were studied by DRIFTS at 423 and 393 K. Sample codes according to the preparation temperature are shown in Table 1.

Appendix Table D1 Sample codes according to the preparation temperature

Catalyst	Method	Preparation temperature (K)
LCO-PC	Pechini	383
PC573	Pechini	573
PC773	Pechini	773
PC823	Pechini	823
LCO-SB	Schiff base	383
SB573	Schiff base	573
SB773	Schiff base	773
SB823	Schiff base	823

Results, Discussion, and Conclusion: IR spectra of the as-prepared gel obtained by the Pechini (LCO–PC) and the Schiff base method (LCO–SB) are shown in Fig. 1(I) and (II), respectively. IR spectra of ligand-PC sample without the metal precursors in Fig. 1(I-a) show a broad band around 3400 cm^{-1} as the characteristic of absorbed water or hydroxyl group in alcohol. The 1736 cm^{-1} band is the C=O stretching of uncoordinated carboxylic group. The bands at 1632 and 1402 cm^{-1}, which shifts to 1609 and 1406 cm^{-1} for LCO–PC in Fig.1(I-b), are contributed to the vibrations of the carbonyl groups, revealing that the carboxylates of citric acid have coordinated with the metal ion precursors. A strong absorption band at 1078 cm^{-1} (1086 cm^{-1}, Nishizawa *et al.*,1997) attributes to the C–O stretching of ethylene glycol in the polymerization process. And the drastic change of IR spectrum at 523 K [Fig. 1(I-e)] can be ascribed to the decomposition and burnout of most of the organics trapped in the gel. The IR band at 1476, 1066 and 844 cm^{-1} (1460, 1060 and 860 cm^{-1}, Yang *et al.*, 2005) reveals the existence of carbonate. At 573 K [Fig. 1(I-f)], the wide absorption band at 584 cm^{-1} due to Co-O bond in the calcined gel is observed, which suggests perovskite formation. For the infrared spectra in Fig. 1(II-a) and (II-b), ligand-SB (without the metal precursors) and LCO–SB, exhibit C=N stretches at 1633 and 1642 cm^{-1}, respectively. A significant shift of this band indicates the coordination of azomethine nitrogen of the Schiff base to the metal ion precursor (Kaczmarek *et al.*, 2004). There are not any obvious changes between 383 – 523 K [Fig. 1(II-b) to

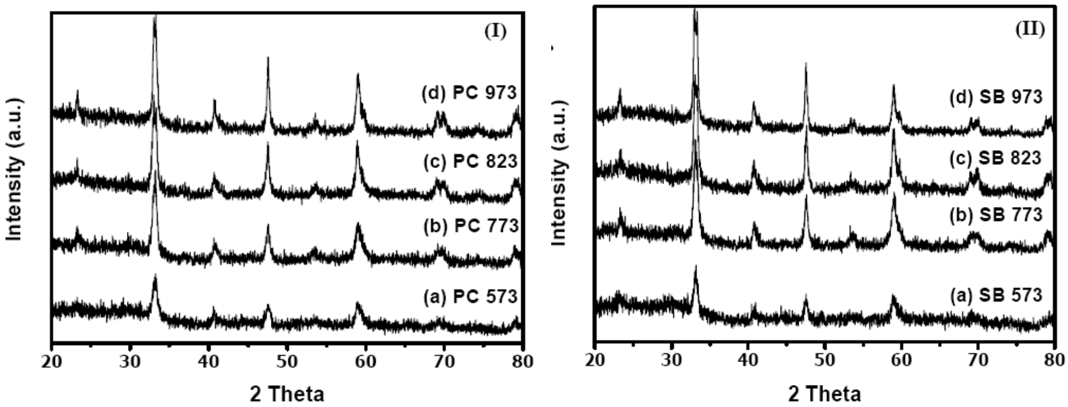
(II-e)]. At 573 K [Fig. 1(II-f)], the bands due to organic compounds disappear. In both methods, when calcination temperature increases to 773 K [Fig 1(I-i) and (II-i)], the carbonate peaks disappear and Co-O stretching doubles at 593, 554 cm^{-1} (596, 552 cm^{-1}, Khalil, 2003). Above 823 K [Fig. 1(I-j) and (II-j)], the products give no longer the IR bands due to carbonate groups and only the characteristic bands of Co-O stretching are observed.



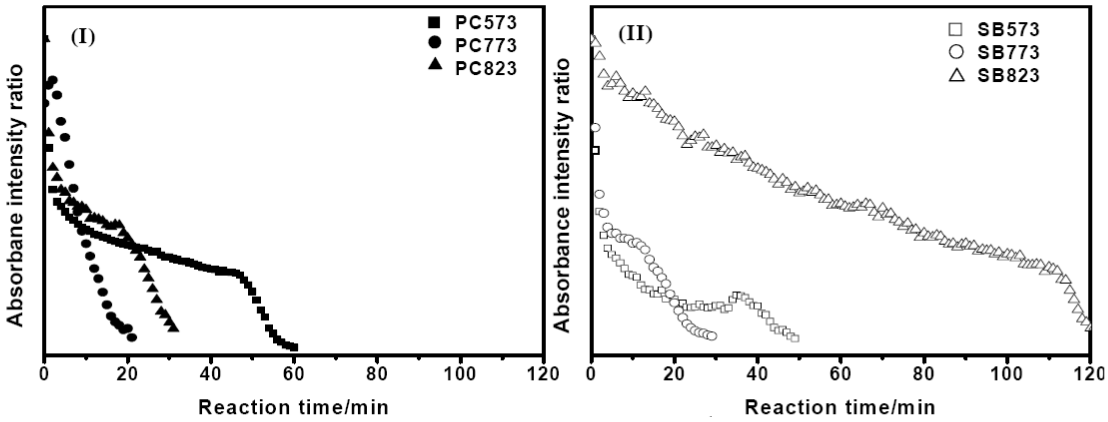
Appendix Figure D1 FTIR spectra of sample prepared by (I)Pechini and (II) Schiff base complex at various temperatures (a) ligand, (b) 383, (c) 423, (d) 473, (e) 523, (f) 573, (g) 623, (h) 773 for 3 h, (i) 773 for 8 h, (j) 823, (k) 873 and (l) 973 K

The XRD patterns for the products obtained from the calcined LCO–PC and LCO–SB are shown in Fig. 2(I-II). When LCO–PC and LCO–SB are subjected to the treatment at 573 K for 3 hours [Fig. 2(I-a) and (II-a), respectively], peaks at 2ϴ

32.90˚, 33.30˚ and 47.50˚ (JCPDS PDF No. 25-1060) due to the rhombohedral $LaCoO_3$ are observed with little trace. At 773, 823 and 973 K [Fig. 2(I-b) to 2(I-d) and 2(II-b) to 2(II-d)] only the peaks due to the $LaCoO_3$ are observed. The crystallite sizes of calcined $LaCoO_3$ from both methods are 7-20 nm (Table 2) calculated by means of x-ray broadening method using Scherrer equations. When the calcination temperature is higher, the crystallite size increases.

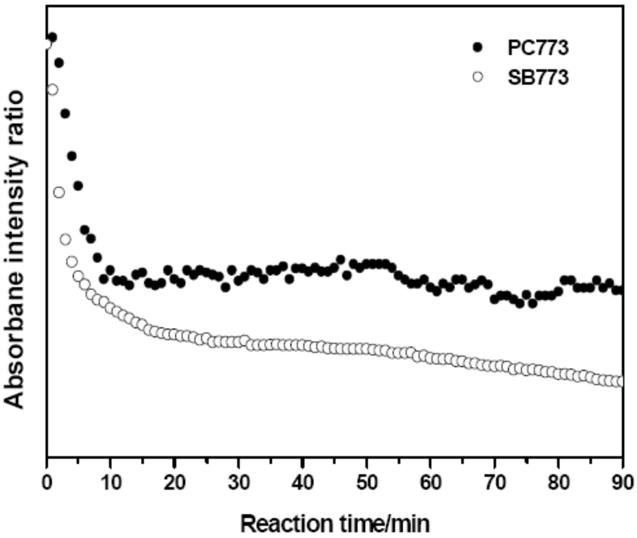


Appendix Figure D2 XRD pattern of (I) LCO-PC and (II) LCO-SB calcined at 573 K for 3 h, 773 K, 823 K and 973 K for 8 h



Appendix Figure D3 Absorbance intensity at wavenumber 2920 cm^{-1} of the unconverted toluene relative to the starting toluene from oxidation at 423 K on (I) ■PC573, ●PC773 , ▲PC823 and (II) □SB573, ○SB773, △SB823 as a function of time

The conversion of the adsorbed toluene as a function of time in the presence of PC-573, 773, 823 and SB-573, 773, 823 are shown in Fig. 3(I-II). The results are shown as the ratio of the toluene absorption band of the actual time related to that of zero time. Of the three catalysts from each method, PC573 and SB573 with the smallest crystallite size (but it still mixed with some impurity) is poorly active. PC773 and SB773 exhibit the activity of the toluene oxidation within 30 min which are faster than the others. From the IR and XRD, the results show that the pure crystalline phase of $LaCoO_3$ is obtained at 773 K. It is concluded that the smaller crystallite sizes of PC773 and SB773 cause higher activity, however impurity can reduces the activity.



Appendix Figure D4 Absorbance intensity at wavenumber 2920 cm^{-1} of the unconverted toluene relative to the starting toluene from oxidation at 393 K on ● PC773 and ○ SB773 as function of time

To compare the effect of both approaches in sol-gel method on the catalytic activity of $LaCoO_3$, the reactions are investigated at 393 K (Fig. 4). SB773 is more active than PC773. It is reported that SB773 has higher ratio of adsorbed oxygen to lattice oxygen than PC773 (Worayingyong *et al*, submitted paper). It can be concluded that $LaCoO_3$ prepared by sol-gel method using the Schiff base complex performed higher catalytic activity than those prepared by the Pechini due to the higher ratio of adsorbed oxygen to lattice oxygen.

Appendix Table D2 The effect of the calcination temperature on the catalytic activity

Catalyst	Crystallite size (nm)	Reaction time (min)
PC573	7.5	60
PC773	12.3	21
PC823	18.5	31
SB573	9.0	49
SB773	13.1	29
SB823	20.1	130

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(3) Yang, W., Chang, Y., Huang, S., (2005) *J. Eur. Ceram. Soc.*, **25**, 3611–3618

(4) Worayingyong, A., Kangvansura, P., Kityakarn, S., Praserthdam P. (submitted paper)

Keywords: $LaCoO_3$, Perovskites, Sol-gel, Pechini, Schiff base.