

Effects of Excess Cobalt Oxide Nanocrystallites on LaCoO_3 Catalyst on Lowering the Light off Temperature of CO and Hydrocarbons Oxidation

Abadian, Layla; Malekzadeh, Azim⁺*

School of Chemistry, Damghan University of Basic Sciences (DUBS), Damghan, I.R. IRAN

Khodadadi, Abbas Ali; Mortazavi Yadollah

Catalysis and Nanostructured Materials Laboratory, School of Chemical Engineering, University of Tehran, Tehran, I.R. IRAN

ABSTRACT: Catalysts with the formula of $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$, where $0 \leq x \leq 1$, were studied for oxidation of CO and C_2H_6 in a synthetic exhaust gas, comprising 6.0 % CO and 0.2 % C_2H_6 in Ar. Ethane was selected as a model for hydrocarbons in the exhaust gas. The performance of catalysts is correlated to their properties, particularly their redox in oxidizing and reducing atmospheres. XRD patterns show perovskite structure for all catalysts. The Co_3O_4 crystallite size was calculated using the Scherrer's equation. TPR results show the reduction of Co_3O_4 and cobalt oxide in perovskite structure in the range of 330 - 475 °C and 550 - 650 °C, respectively. Disappearance of the cobalt oxide structure in XRD patterns of $\text{LaCo}_{(1 \leq x \leq 1.3)}\text{O}_{(3+\delta)}$ catalysts are attributed to small size of the cobalt oxide crystallites. Redox properties of catalysts were also studied by electrical conductivity measurements. Similar Arrhenius-type electrical conductivity behaviors of catalysts with that of cobalt oxide indicates that the cobalt component is essential for charge carrier mobility in $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts. Catalyst with 0.3 mole excess cobalt, i.e. $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$, which shows the lowest activation energy of electrical conductivity (E_a) and the lowest ratio of conductivities in reducing to oxidizing atmospheres, has the lowest light off temperatures for oxidation of both CO and ethane. High ability of catalysts in gas phase-lattice oxygen transfer is evidenced by the fast reduction and oxidation behaviors of catalysts in CO and air atmosphere, respectively.

KEY WORDS: Mixed oxides, Perovskite, LaCoO_3 , Co_3O_4 , CO, Hydrocarbon, Exhaust gas, Catalytic converter, Oxidation, Conductivity, Cold start, Nanocrystallites oxide, Light off temperature.

INTRODUCTION

About 80 % of the pollutants of a car engine can account for the first sixty to ninety seconds of operation

after a cold-start. Relatively high temperature (light-off temperature) is needed to meet standard emissions at this

* To whom correspondence should be addressed.

+ E-mail: malekzadeh@dubs.ac.ir

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time. The main reason is the sluggish catalytic activity at low temperatures. Efforts for heating the catalytic converter have all encountered difficulties, including cost, complexity, and durability [1]. Varieties of approaches have been also investigated to reduce cold-start emissions due to increasingly strict emission standards [2].

Mixed metal oxides comprise the vast majority of catalysts used in modern chemical industry. Among the mixed metal oxides, perovskite-type oxides with the formula ABO_3 are considered important due to their prominent activities [3-7]. Perovskite-type oxides are considered of great interest as an environmentally friendly and cheap catalyst. Perovskites of $LaMO_3$ ($M=Mn, Co, Fe$ and Ni), with M at octahedral sites (B) and lanthanum ion at tetrahedral positions (A) in ABO_3 perovskite formula, are of interest for the catalytic redox reactions associated with the pollutants gases emitted from vehicles [8,9]. Solid-state reaction of La- and Co-oxides at high temperature of about 927 °C results in the formation of large particle size and limited degree of chemical homogeneity.

Fine and homogeneous particles with high specific surface area are formed during a chemical solution process, such as citrate method, using different starting precursors, usually nitrate and an organic additive such as citric acid [10].

XRD patterns of the perovskite oxides $LaCoO_3$ that was prepared from sol-gel method (Pechini method) showed $LaCoO_3$ and small amount of Co_3O_4 after calcinations at 850 and 1100 °C [11]. Reduction patterns of the perovskites that was prepared by Pechini method showed that the perovskites are reduced in two zones; the first in the range of 350-500 °C and the second one in the range of 500-700 °C [12]. Low temperature peak was detected to belong to the amorphous cobalt oxides reduction [12].

Significant oxygen ionic conductivity/mobility with prevailing electrical conduction was reported for perovskite-type lanthanum cobaltite, $LaCoO_3$, especially after suitable compositional modifications [13,14]. Transfer of charge carriers via Co-O-Co bonds was reported to be responsible for the electrical conduction in lanthanum cobaltite [15]. Diffusion of oxygen ions in $LaCoO_{(3-\delta)}$ occurs via a vacancy mechanism [15]. The temperature dependence of the oxygen vacancy diffusion

coefficient in $LaCoO_{(3-\delta)}$ single-crystals, determined by the isotopic method, can be approximated by [3]:

$$D_V (\text{cm}^2\text{s}^{-1}) = 2.30 \times 10^{-2} \times e^{-\frac{77 \pm 21 \text{kJmol}^{-1}}{RT}}$$

Oxygen nonstoichiometry of lanthanum cobaltite also was reported to increase regularly with decreasing oxygen partial pressure, being almost proportional to $P_{O_2}^{1/2}$ [3].

Perovskite oxides based on ABO_3 type, especially with rare earths, have been considered the most promising three-way catalysts as the substitute of the traditional noble metal catalysts and catalytic combustion catalyst for the purification of automotive pollutants. However, there are many unsolved problems with perovskite-based catalysts, such as catalytic activity, thermal stability and resistance to potential poisons in fuel or from oil additives such as P, S and Cl. For example the lubricating oil, which is indispensable for wear protection of the mechanical parts of engines, has deleterious phosphorous poisoning impact on catalyst activity [16]

In this work, catalytic performances of cobalt oxide added $LaCoO_3$ system, i.e. $LaCo_{(1+x)}O_{(3+\delta)}$, were studied for the light-off temperature of CO and C_2H_6 oxidation. Here x is 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0. Effect of excess cobalt oxide on the structural, redox and electrical properties of prepared catalysts were also studied. A comparison was also taken place with pure lanthanum and cobalt oxides as references.

EXPERIMENTAL

Catalyst preparation

All $LaCo_{(1+x)}O_{(3+\delta)}$ samples, where x is 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0, were prepared by the so-called citrate method in a way almost identical to that reported by *Alifanti, M. et al.* [17]. In brief, a solution of appropriate moles of the corresponding metal nitrates and citric acid equivalent with nitrate ions moles was evaporated at 60 °C for 6 h. The obtained viscous sample was subsequently dried at 80 °C overnight. The resulting spongy and friable pink material was powdered and was kept at 150 °C overnight. The resulting spongy, friable brown material was powdered and calcined at 600 °C for 12 h.

Table 1: Temperatures for 10, 50 (light off) and 90 % oxidation of CO and C₂H₆ on La₂O₃, Co₃O₄ and LaCo_(1+x)O_(3+δ) catalysts. Here x is 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0.

Catalyst	Temperatures for different % CO conversion (°C)			Temperatures for different % C ₂ H ₆ conversion (°C)		
	10 mol %	50 mol %	90 mol %	10 mol %	50 mol %	90 mol %
La ₂ O ₃	280	340	401	351	498	680
Co ₃ O ₄	156	160	164	232	343	443
LaCoO ₃	148	156	165	245	330	440
LaCo _{1.1} O _{3+δ}	128	147	157	272	325	390
LaCo _{1.2} O _{3+δ}	120	140	143	228	315	350
LaCo _{1.3} O _{3+δ}	115	117	120	190	300	320
LaCo _{1.4} O _{3+δ}	132	139	141	250	360	434
LaCo _{1.5} O _{3+δ}	137	143	151	270	365	440
LaCo _{1.7} O _{3+δ}	141	146	155	280	372	455
LaCo ₂ O _{3+δ}	148	166	175	300	385	472

Performances tests

CO and C₂H₆ oxidation tests over the catalysts was studied in an experimental set-up using a quartz tube reactor, filled with 200 mg of 60-120 mesh sized catalyst supported on a quartz wool. In a typical experiment, a mixture of 6.0 % CO and 0.2 % C₂H₆ in Ar was combined with a stoichiometric amount of air, as the synthetic exhaust gas of gasoline engines, was passed through the catalyst bed with a total gas mixture flow rate of 40 mL/min at STP. Catalytic tests were carried out by raising the catalyst bed temperature from 50 °C to complete ethane oxidation temperature (500-700 °C; see table 1). The product stream containing carbon monoxide, ethane and carbon dioxide was analyzed by an on-line multi-valve, multi-column gas chromatograph (GC) with a FI detector equipped with a methanizer. No carbon dioxide was detected using an empty reactor equipped with the quartz wool. (Comment 4) No byproducts, such as ethylene that is the product of the partial oxidation of ethane, was detected.

Powder X-ray Diffraction Studies

X-ray diffraction patterns of the freshly calcined catalysts were recorded in an X'Pert diffractometer (Philips, Holand) with Cu-K α radiation ($k=0.15418$ nm) filtered by a copper tube and operated at 50 kV and 40 mA. Diffraction patterns were recorded in the range of $2\theta = 20-80^\circ$ with a step of 0.02 and a time per step of 1s.

Temperature Programmed Reduction Studies

The reducibility of freshly calcined catalysts was characterized by the temperature-programmed reduction technique using a conventional temperature programmed reduction-oxidation apparatus, (CHEMBET-3000) from Quanta Chrome Corporation. A gas stream of 7 % H₂ in nitrogen with the flow rate of 10 mL/min through a quartz U tube containing 20 mg of catalyst was used for TPR analysis. Reduction treatment was then carried on from room temperature to 900 °C at a heating rate of 10 °C/min.

DC Electrical Conductivity Measurements

The direct current electrical conductivity of various catalysts was measured using an electrical conductivity measurement set-up equipped with a home-made cell presented in Fig. 1. In each electrical conductivity measurement, 200 mg of 60-120 mesh sized sample was placed between the two 24 K gold electrodes on quartz wool (see Fig. 1). The electrical conductivity measurements were carried out during heating the catalyst in air atmosphere from ambient temperature to 200 °C by continually increasing the temperature. Electrical conductivity data reported here are the values measured under isothermal steady state conditions at each temperature. The electrical conductivity studies were also carried out during the switching of the gases from air atmosphere to Ar to 6 % CO in Ar, as reductant, and to air, as oxidant, at 200 °C

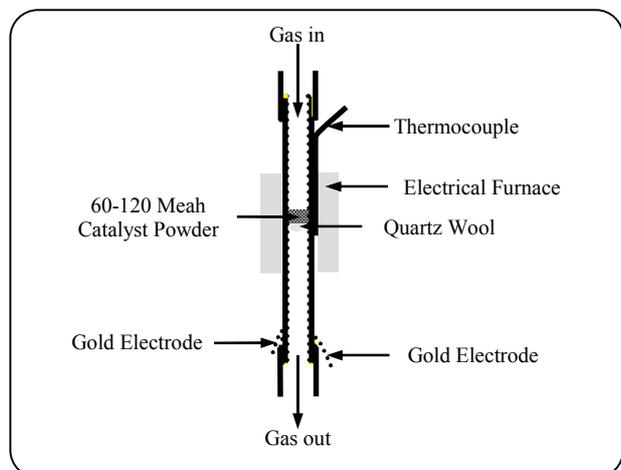


Fig. 1: Experimental home-made cell that was used for electrical conductivity measurement of catalysts.

(air \rightarrow Ar \rightarrow 6 % CO in Ar as reductant \rightarrow air as oxidant). Reported electrical conductivity (σ) is the reciprocal of the catalyst resistance, R_{cat} , which was calculated using following formula:

$$R_{\text{cat}} (\Omega) = \frac{R_{\text{var.}}}{V_{\text{var.}}} (V - V_{\text{var.}})$$

where $V_{\text{var.}}$ is the voltage between two gold electrodes inserted in the catalyst bed (see Fig. 1). $V_{\text{var.}}$ was continuously monitored by a data acquisition system including a A/D converter and equipped to a variable resistances ($R_{\text{var.}}$). The DC power supply voltage (V) was fixed at 4.1 V throughout the experiments.

RESULTS AND DISCUSSIONS

Catalytic Oxidation

The temperatures at which 10, 50 (light off temperature), and 90 % conversion of CO and ethane in a stoichiometric amount of air occurs on the La_2O_3 , Co_3O_4 and $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts are shown in Table 1. Ethane was selected as a model for hydrocarbons in the exhaust gas. Air was added to the CO and ethane gas mixture to prepare the synthetic exhaust gas that corresponds to the stoichiometric air to fuel ratio.

Of all catalysts, La_2O_3 shows the lowest activity for conversion of both CO and ethane. Although the LaCoO_3 shows about the same activity as Co_3O_4 catalyst, it is more stable [18]. No decreasing in catalytic activity was observed over $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts after 100h on stream. As more excess cobalt up to 0.3 mole is added to

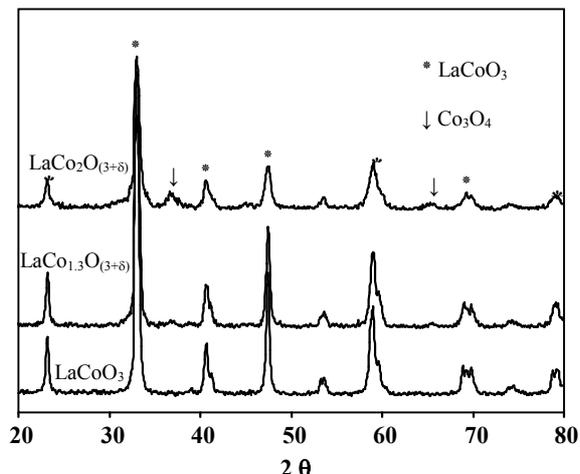


Fig. 2: XRD patterns of LaCoO_3 , $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ and $\text{LaCo}_2\text{O}_{(3+\delta)}$ catalysts freshly calcined at 600 °C.

the LaCoO_3 catalyst, the oxidation light-off temperature of both CO and ethane reduces to a minimum value of 117 and 300 °C, respectively. When 0.1 mole more cobalt is added to the $\text{LaCo}_{1.3}\text{O}_{3+\delta}$ catalyst [corresponding to $\text{LaCo}_{1.4}\text{O}_{(3+\delta)}$] the light off temperatures sharply increases. Further addition of the excess cobalt to the LaCoO_3 up to 1.0 mole gradually increases the oxidation temperatures of CO and ethane.

Catalyst Structural Features

Representative XRD diffraction patterns of freshly calcined LaCoO_3 , $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ and $\text{LaCo}_2\text{O}_{(3+\delta)}$ catalysts are shown in Fig. 2. XRD patterns of catalysts containing 0.1 and 0.2 mole excess cobalt is similar to the LaCoO_3 catalyst (data not shown). As Fig. 2 shows, Co_3O_4 phase is observed for catalysts containing ≥ 0.3 mole excess cobalt. No Co_3O_4 peaks appeared by increase in the calcination temperature of LaCoO_3 , $\text{LaCo}_{1.1}\text{O}_{(3+\delta)}$ and $\text{LaCo}_{1.2}\text{O}_{(3+\delta)}$ catalysts up to 1000°C. Therefore, absence of Co_3O_4 crystalline phase in catalysts containing less than 0.3 moles excess cobalt can be attributed to low concentration and/or amorphous structure of cobalt oxide [12]. According to the XRD results, $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts can be regarded as Co_3O_4 supported on lanthanum cobaltite, i.e. $\text{Co}_3\text{O}_4/\text{LaCoO}_3$. Using Sherrer's equation [19] for XRD peak at $2\theta = 33^\circ$, the average sizes are in range of 20–23 nm for LaCoO_3 , $\text{LaCo}_{1.3}\text{O}_{3+\delta}$, and $\text{LaCo}_2\text{O}_{3+\delta}$ catalysts, respectively. The same calculations at 2θ of 37° show that crystallite sizes of Co_3O_4 in $\text{LaCo}_2\text{O}_{3+\delta}$ catalyst is 9 nm. The broadening peak of 37°

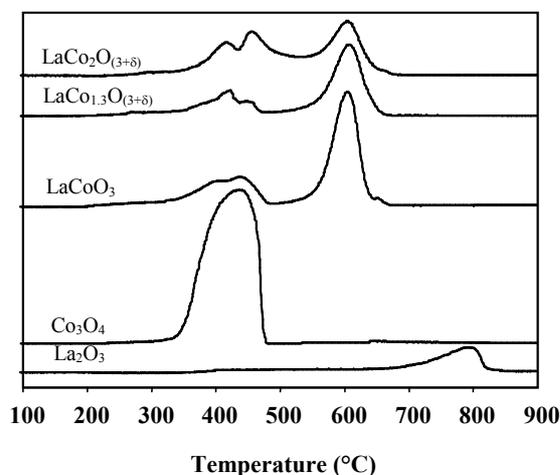


Fig. 3: Temperature programmed reduction patterns of La_2O_3 , Co_3O_4 , LaCoO_3 , $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ and $\text{LaCo}_2\text{O}_{(3+\delta)}$ catalysts.

in LaCoO_3 and $\text{LaCo}_{1.3}\text{O}_{3+\delta}$ samples is evidence for the smaller crystallite size of Co_3O_4 in these catalysts. The nanocrystallites of Co_3O_4 may be responsible for enhanced activity of cobalt lanthanate catalysts containing excess cobalt oxide.

Catalysts Temperature Programmed Reduction

Results of TPR analysis of La_2O_3 , Co_3O_4 , LaCoO_3 , $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ and $\text{LaCo}_2\text{O}_{(3+\delta)}$ catalysts are shown in Fig. 3. The reduction peak of La_2O_3 appears at temperatures higher than 700°C , while the cobalt oxide reduces in the range of $330\text{--}475^\circ\text{C}$. Two cobalt oxide reduction patterns are observed in LaCoO_3 TPR. One corresponds to the Co_3O_4 reduction in the range of $330\text{--}475^\circ\text{C}$ and the other for reduction of cobalt oxide in perovskite structure in the range of $550\text{--}650^\circ\text{C}$. Compared with the pure cobalt oxide, similar peak position shows that the similar cobalt ion species exist in both lanthanum cobalt oxide and purer Co_3O_4 samples. The double peaks of Co_3O_4 reduction in the range of $330\text{--}475^\circ\text{C}$, however, indicate stepwise reduction of Co_3O_4 in lanthanum cobalt oxide catalysts. Appearance of stepwise reduction of cobalt oxide in $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts is evidence for some interaction of the Co_3O_4 and perovskite structure. TPR result of LaCoO_3 sample shows that some of cobalt cations are not in the perovskite structure and exist in the form of a separate phase of Co_3O_4 . Ratio of the two reduction peaks of cobalt oxide in form of Co_3O_4

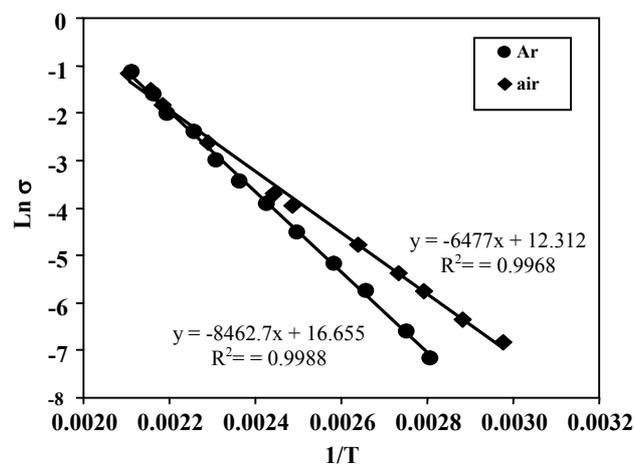


Fig. 4: Electrical conductivity variations with temperature for LaCoO_3 catalyst in air atmosphere (oxidation conditions) and also Ar atmosphere (inert conditions) from ambient temperature to 200°C .

($350\text{--}480^\circ\text{C}$) and in the perovskite structure ($550\text{--}650^\circ\text{C}$) is also observed to increase with the excess cobalt in $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ series of catalysts (see Fig. 3).

According to the XRD and TPR results (Figs. 2 and 3), disappearance of the Co_3O_4 peak in XRD pattern of LaCoO_3 sample can be attributed to the crystallite size of Co_3O_4 . It can be concluded that there are some cobalt cation vacancies in LaCoO_3 perovskite structure. It imposes some oxy anion variations in the perovskite structure; in form of O^{2-} or vacancies.

Electrical Conductivity Studies

Fig. 4 shows the electrical conductivity results of freshly calcined LaCoO_3 sample at different temperatures from ambient to 200°C in air (oxidizing) and Ar (inert) atmospheres. An exponentially increase of the electrical conductivity with temperature, denoted as electrical conductivity behavior, is observed in both atmospheres. The electrical conductivity values of LaCoO_3 catalyst, however, depend on the atmosphere at its lower values.

Similar electrical conductivity behaviors were observed for all catalysts containing excess cobalt oxide, i.e. $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$, pure Co_3O_4 sample and also spent catalysts during heating the catalysts from ambient temperature to 200°C in air and Ar atmospheres, respectively (data not shown). No electrical conductivity was observed for La_2O_3 sample under these conditions. The results show that the cobalt oxide in form of Co_3O_4

Table 2: E_c^a , σ_{Ar}^b , σ_{air}^b and σ_{CO}^b for La_2O_3 , Co_3O_4 and $LaCo_{(1+x)}O_{(3+\delta)}$ samples.

Catalyst	$La_2O_3^c$	Co_3O_4	$LaCoO_3$	$LaCoO_3^d$	$LaCo_{1.1}O_{(3+\delta)}$	$LaCo_{1.2}O_{(3+\delta)}$	$LaCo_{1.3}O_{(3+\delta)}$	$LaCo_{1.4}O_{(3+\delta)}$	$LaCo_{1.5}O_{(3+\delta)}$	$LaCo_{1.7}O_{(3+\delta)}$	$LaCo_{2.0}O_{(3+\delta)}$
E_c (conductivity) (kJ/mol)	-	73	55	70	64	60	52	56	59	69	70
σ_{Ar}/σ_{air}	-	1	1	-	1	1	1	1	1	1	1
$\sigma_{CO}/\sigma_{air} \times 10^3$	-	64	62	-	51	52	28	32	66	70	71

a) E_c , activation energy of the electrical conductivity, were obtained from the exponential increase of the electrical conductivity with temperature up to 200 °C in air atmosphere ($\sigma = \sigma_0 e^{-E_c/RT}$, see Fig. 4). b) σ_{Ar} , σ_{air} and σ_{CO} are conductivity of catalysts that are obtained in different atmospheres of air, Ar and 6.0 % CO in Ar at 200 °C, respectively (see Fig. 5). c) no conductivity were observed for La_2O_3 catalyst under these conditions. d) in Ar atmosphere.

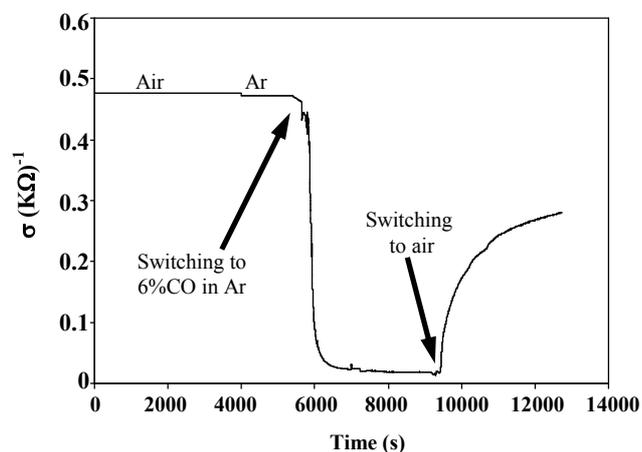


Fig. 5: Electrical conductivity variations during switching of the atmosphere from air to Ar to 6.0 % CO in Ar back to air (air → Ar → 6.0 % CO in Ar → air) at 200 °C.

(Co II and Co III) or in perovskite structure (Co III) is essential for electrical conductivity and also catalytic performances of $LaCo_{(1+x)}O_{(3+\delta)}$ samples.

Table 2 shows the activation energy of the electrical conductivity (E_c) obtained from electrical conductivity behavior of Co_3O_4 and $LaCo_{(1+x)}O_{(3+\delta)}$ catalysts during the temperature raising in air ($\ln\sigma = -E_c/RT + \ln\sigma_0$). The catalyst with 0.3 mole excess cobalt [$LaCo_{1.3}O_{(3+\delta)}$] and with the lowest activation energy of the electrical conductivity shows the best catalytic performance among the La_2O_3 , Co_3O_4 and $LaCo_{(1+x)}O_{(3+\delta)}$ catalysts (see tables 1 and 2). No reaction or conductivity changes were observed with the quartz reactor filled with the quartz wool without the catalyst (blank run). These results show

that the catalyst provides a suitable path for the oxygen and electron transfer to/from adsorbed species on catalyst surface. Addition of excess cobalt ion up to 0.3 mole improves the path of oxy-anion and electron transfer, improving the oxidation activity of the catalysts (see tables 1 and 2). Cobalt oxide with the similar catalytic performance as $LaCoO_3$ catalyst but different E_c can not be considered as a reference due to different structure that is spinel for cobalt oxide.

Reducibility and oxidizability properties of catalysts were studied by electrical conductivity measurements in different atmospheres. For this, electrical conductivity of catalysts was measured during the switching of the gases flow on the catalyst from air atmosphere to Ar to 6.0 % CO in Ar to air (air → Ar → 6 % CO in Ar → air) at 200 °C. Results for the $LaCo_{1.3}O_{(3+\delta)}$ sample are shown in Fig. 5. No change has taken place in the charge carrier concentration/mobility during the switching from air (oxidizing) to Ar (inert) atmospheres at 200 °C. Results show that the catalysts are oxygen rich and do not gain and lose oxygen in air and Ar atmosphere at 200°C, respectively. Comparison of the catalyst electrical conductivity in air and Ar atmospheres shows that the mobile oxy anions, which are the main charge carriers, are strongly stable (see Figs. 4 and 5). Depletion of charge carriers, however, sharply takes place in switching from Ar atmosphere to 6.0 % CO in Ar as a reducing atmosphere (Fig. 5). Electrical conductivity slowly increases to its first level by switching back to air (see Fig. 5). Results indicate that the mobile oxy anions are the main part of charge carriers and the electrical

conductivity is a bulk property of the catalysts. Similar electrical conductivity behavior were observed for all Co_3O_4 and $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ samples under these conditions (data not shown). No electrical conductivity is observed for the La_2O_3 under these conditions. Results show that the cobalt oxide has critical effect on electrical and redox properties and also catalytic performance of $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ samples. Fast reduction and oxidation of catalyst during the switching of the conditions from Ar to reducing CO and then oxidizing air atmosphere shows that the catalysts are suitable for giving and gaining oxygen under reducing and oxidizing conditions, respectively (see Fig. 5). This property makes the catalysts active for oxidation of adsorbed species on the catalyst surface.

Electrical conductivity data under reducing and oxidizing conditions are reported as the ratio of $\sigma_{\text{CO}}/\sigma_{\text{air}}$ for La_2O_3 , Co_3O_4 and $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts in table 2. Here σ_{air} and σ_{CO} are catalyst electrical conductivity values under air and 6.0 % CO in Ar atmospheres at 200 °C, respectively. The lowest $\sigma_{\text{CO}}/\sigma_{\text{air}}$ corresponds to the $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ catalyst, which also shows the lowest light off temperatures for both CO and ethane oxidation (see tables 1 and 2). The $\sigma_{\text{CO}}/\sigma_{\text{air}}$ may indicate the catalyst capability of transferring oxygen to reducing species such as CO and C_2H_6 adsorbed on the catalyst surface.

CONCLUSIONS

LaCoO_3 catalysts with excess cobalt oxide were studied for oxidation of CO and C_2H_6 in a synthetic exhaust gas of gasoline engines. The oxidation performance of the catalysts is correlated to their properties, particularly their electrical conductivity in oxidizing and reducing atmospheres.

An increase in the cobalt oxide concentration in LaCoO_3 perovskite up to 1.3 moles improves the electrical conductivity, redox property and oxidation activity of the catalyst. Excess cobalt oxide is shown to be in form of Co_3O_4 phase. The $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts can be considered as Co_3O_4 nanocrystallites supported on LaCoO_3 . $\text{LaCo}_{(1+x)}\text{O}_{(3+\delta)}$ catalysts are observed to be flexible samples with respect to the redox process. Catalyst with the formula of $\text{LaCo}_{1.3}\text{O}_{(3+\delta)}$ was observed to provide a better path for electron and gas phase oxygen transfer from and to the adsorbed species on catalyst surface, respectively, showing a better oxidation property (lower oxidation temperature).

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