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Production of perovskite catalysts on ceramic monoliths with nanoparticles for dual fuel system automobiles

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ABSTRACT: (Lanthanum, Cerium)(Iron, Manganese, Cobalt, Palladium)$(Oxygen)_3$- Perovskite catalyst was prepared by the citrate route and deposited on ceramic monoliths via dip coating procedure. The catalyst was applied on a car with XU7 motors and the amount of emission was monitored with vehicle emission test systems in Sapco company. The results were compared with the imported catalyst with noble metals such as palladium, platinum and rhodium by Iran Khodro company based on the Euro III standards. The catalysts were characterized by specific surface area measurements, scanning electron microscopy, X-ray diffraction, line scan and map. In the results, obtained in the home made sample, the amount of carbon monoxide, nitrogen oxides and hydrocarbons were lower than imported catalyst with Iran Khodro company with nobel metals. The illustration shows nano particles size on coat. The microstructure evaluation showed that the improved properties can be related to the existence of nano particles on coating.

Key words: *Air pollution, carbon monoxide, nitrogen oxides, hydrocarbons, emissions, X-ray diffraction, line scan*

INTRODUCTION

One of the main sources of air pollution in large cities is automotive exhaust gas emissions. Therefore, catalytic converters have been applied for exhaust gas treatment since the 1970s. Conventional three-way automotive exhaust catalysts contain precious metals palladium (Pd), platinum (Pt) and rhodium (Rh) for treatment of pollutants such as carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NOx), (Heck and Farrauto, 1995). One of the reasons of deterioration of these catalysts is considered to be due to the decrease in active surface area of precious metals caused by grain growth in high temperature redox (reduction–oxidation) fluctuations of the exhaust gas. To compensate for this deterioration, conventional catalysts are loaded with excess amounts of precious metals (Nishihata *et al.*, 2005). The increasing prices of noble metals such as Pt, Rh and Pd driven partly by the large demand of the automotive industry motivates the investigation of material concepts to reduce the precious metal content in automotive catalysts (Mondragon Rodriguez *et al.*, 2008). Perovskite-type oxides have general formula as ABO_3 in which A is a rare earth or alkaline earth metal and B is a transition metal and these oxides are typically *p*-type semiconductors. Their composition can be varied in a wide range by partial substitution of lower valent cation in A or B site yielding additional mobile anion vacancies. Their mixed conductivity by both ion and electron migration and their high nonstoichiometric composition have been resulted from the basis of the applications of this group of materials in these areas such as electrochemistry (Kharton *et al.*, 1999; Cheng *et al.*, 2005) catalysis (Leontiou *et al.*, 2003; Tao and Irvine, 2004; Liu *et al.*, 2007) solid oxide fuel cells (Skinner, 2001; Uhlenbruck and Tietz, 2004) oxygen separation membranes (Takamura *et al.*, 2004) chemical sensors for the detection of humidity (Holc *et al.*, 1995) alcohol (Kong and Shen, 1996) and gases such as oxygen

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(Lukaszewicz *et al.,* 1990), hydrocarbon (Brosha *et al.*, 2000) and nitric oxide (Traversa *et al.*, 1995). Earlier studies reported on perovskite oxide $LaCo_xFe_{1"x}O_3$ mainly involved methane oxidation catalysis (Szabo *et al*., 2003; Royer *et al*., 2004; Royer *et al*., 2005a, 2005b; Goldwasser *et al*., 2005). Incorporation of small amounts of precious metals into a perovskite structure can prevent their sintering, reduce losses due to volatilization at high operating temperatures and avoid reactions with the support that show the catalyst deactivation. Recent attention has been concentrated on the use of palladium based catalyst for TWC (three-way catalyst) formulation. Pd is well known to have a good resistance to thermal sintering, lower price than Pt and Rh and also have a good activity for oxidation of CO and hydrocarbons (Rainer *et al*., 1997; Beck *et al*., 1997; Van Yperen *et al*., 1998).

The $LaFe_xCo_{(1"x)}O_3$ perovskite with ABO_3 type structure is formed with La-atoms at the A-site coordinated with 12 oxygen and with iron (Fe) and cobalt (Co) at the B-site coordinated with six oxygen atoms. The $LaFeO_3$ is orthorhombic and the $LaCoO_3$ is rhombohedral (Mondragon Rodriguez *et al.,* 2008). $LaCoO_3$ is particularly attractive because it is one of the most reducible ABO3-type perovskites (Nakamura *et al.,* 1979) and displays a rich phase behavior under reducing conditions (Hansteen *et al.*, 1998; Huang *et al.,* 2005) which can be significantly influenced on addition of a noble metal such as Pd, Pt and Rh (Engelmann-Pirez *et al.*, 2005; Cimino *et al*., 2006). The tolerance factor $(t) = (rA + rO)/\sqrt{2}\times(rB + rO)$ is one requirement to form a perovskite structure and must lie between $0.8 < t < 1.0.2$. Due to this tolerance wide, variety of elements can be combined without change in the original structure. Precious metals such as Pd, Pt, Rh can also be incorporated into the crystal lattice. In the present study, the (La-Ce)(Fe, Mn, Co, Pd)O_3– perovskites coating on ceramic monoliths were prepared by a dip coating procedure.

MATERIALS AND METHODS

Preparation of catalysts with ceramic monoliths

(La-Ce)(Fe, Mn, Co, Pd)O_3-Perovskite catalyst was prepared by the citrate method. The following materials were used in appropriate quantities and dissolved in distilled water $Al(OH)_3$ (Merck), $La(NO_3)_3.6H_2O$ (Merck),$Mn(NO_3)_2$. $4H_2O$(Merck), $Ce(NO_3)_3$. $6H_2O$ (Merck), Co $(NO_3)_2$. $6H_2O$ (Merck), $Pd(NO_3)_2.xH_2O$ (Merck) and $FeCl_2$ (Merck). Citric acid monohydrate (Merck, 99.5 %) were used as starting materials. Aqueous solution with cation ratio La: (Fe,Co,Ce,Pd) of 1: 3, 3.5, 0.4, 10.28 was prepared and dissolved in 1.50 L distilled water. The citric acid was added in 10 wt.% excess over the stoichiometric quantity (14.01 g of $C_6H_8O_7.H_2O$) to insure complete complexation of the metal ions. Then, solution was stirred for 1 h. The pH was regulated by adding hydrochloric acid (HCl) and was reduced from 6.6 to 3.2 to reach best suspension. Materials were coated on two ceramic monoliths that made with cordierite phase $Mg_2Al_4Si_5O_{18}$ with cylinder length (5 cm), internal diameters (8 cm), external diameter (12 cm), wall thickness (0.9 mm) and geometric specific surface 23.555 q.m/gr. Both monoliths were dipped in the resulting solution and then were heating at 407 K (134 °C). The precursor was finally calcined in air at 760 °C for 3 h to obtain the perovskite oxides.

Dip coating technique

The dip coating technique was applied as follows: The monolith was dipped and withdrawn in slurry at constant speed (12 cycles/min) for 30 min. The monolith was hung and kept in the channels, direction perpendicular to the surface of the slurry during the whole dipping and withdrawing processes. Each dipping was followed by the removal of the excess of slurry by dry air and a subsequent heating at 407 K (134 °C) for 30 min. The coating and heating procedures were repeated several times until the desired loading obtained few microns. Finally, the ceramic monoliths were calcined at 1033K (760 °C) for 3 h.

Canning and catalytic testing

The catalyst canning was conducted in Tarabgin company Mat at Mashhad-IranKhodro factory and then fixed under Rd car in Sapco-Irankhodro workshop for the vehicle emission test systems (AVL).

Catalyst characterization

Phase identification of the fresh catalysts was carried out by X-ray diffractometry using a computerized SEIFERT/PTS 3003 X-ray diffractometer (Cu Ka radiation, λ 1.54 A° by Ni filter).

Diffractograms were recorded with a step scan of 0.1 for 2θ between 0° and 80°. Scanning electron microscopy (SEM), line scan and map were performed by a Vega 2XMU/ Tescan instrument to investigate the crystal size and morphology, as well as the elemental composition of the catalysts.

RESULTS AND DISCUSSION

Emission percentage

Table 1 and 2 show the emission percentage of prepared catalyst and Iran Khodro company's catalyst with Euro III standards and with gas fuel and gasoline fuel, respectively.

The data indicated that (La-Ce)(Fe,Co,Pd)O_3 Perovskite catalyst had lower emission when gas fuels (methane combustion), reduced CO, HC and NOx were more than Iran Khodro imported catalysts. The results indicated that when the gasoline fuels were applied, the data was approximately the same.

X-ray diffraction (XRD)

The diffractograms of (La-Ce) (Fe,Co,Pd)O_3 coated on ceramic monoliths are displayed in Fig. 1. X-ray diffraction shows the following phases: $[((Mg,Fe)_2Al_4Si_5O_{18})]$, $(LaCo_{0.4}Fe_{0.6}O_3)$, (La_2PdO_4), $(Ce_3Pd_{20}Si_6)$ and $[((Mg_{0.86}Fe_{0.14})(Ce_{0.5}La_{0.5})_2(CO_3)_4)]$.

From the results, one can concluded that the crystal structure of perovskite-type can be obtained in all concentration ranges of Co and Co can substitute for Fe limitlessly to form $LaCo_xFe_{1-x}O_3$ solid solution. As it is known, an ionic radii rule is required to form perovskite structure, i.e. the so-called tolerance factor (*ft*) defined by the equation:

$$ft = (rA + rO) / 2(rB + rO)$$

Where, $0.75 < ft < 1.0$. *r*A, *r*B and *r*O are the ionic radii of A, B and the oxygen anion, respectively. Because the ionic radii of CO^{2+} and Fe^{3+} are 0.074 and 0.064 nm, respectively (Zhuyi Wang *et al.*, 2008), this slight difference makes the perovskite structure to be maintained within tolerance factor.

Since the microstructure of the substituted perovskite contains no more Pd-particles, it can be postulated that the reoxidation treatment of the reduced $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ causes the reversible incorporation of Pd ions into the crystal structure of the perovskite (Mondragon Rodriguez *et al.*, 2008).

Scanning electron microscopy (SEM)

The SEM micrograph (Figs. 2 and 3) of (La-Ce)(Fe,Co,Pd)O_3 shows that surface of the ceramic monoliths were completely covered on the surface of coat. Size of the pores were uniform (1–5 µm) and the size of particles were between 5 to 90 nm. The SEM micrograph, map (Fig. 4.) and line scan (Figs. 5 and 6)

Table 1: The emission percentage of prepared catalyst and Iran Khodro Company catalyst with gas fuel (λ =Stoichiometric point–air/fuel ratio)

Parameters	Emission percentage of catalyst after 15 min	Emission percentage of catalyst at first	Emission percentage of Iran Khodro catalyst after 15 min	Emission percentage of Iran Khodro catalyst at first
λ	1.019	1.025	1.024	1.039
CO	0.180	0.340	0.360	0.510
CO_2	12.60	12.20	11.90	11.80
O_2	0.550	0.710	0.820	0.990
HC	52	63	64	71
NOx	19	26	22	29

Table 2: The emission percentage of prepared catalyst and Iran Khodro Company catalyst with gasoline fuel (λ =Stoichiometric point–air/fuel ratio)

Parameters	Emission percentage of catalyst after 15 min	Emission percentage of catalyst at first	Emission percentage of Iran Khodro catalyst after 15 min	Emission percentage of Iran Khodro catalyst at first
λ	1.015	1.016	1.015	1.016
CO	0.430	0.540	0.450	0.560
CO_2	15.40	15.10	15.40	15.10
O_2	0.530	0.540	0.550	0.580
HC	51	52	51	53
Nox	23	24	22	24

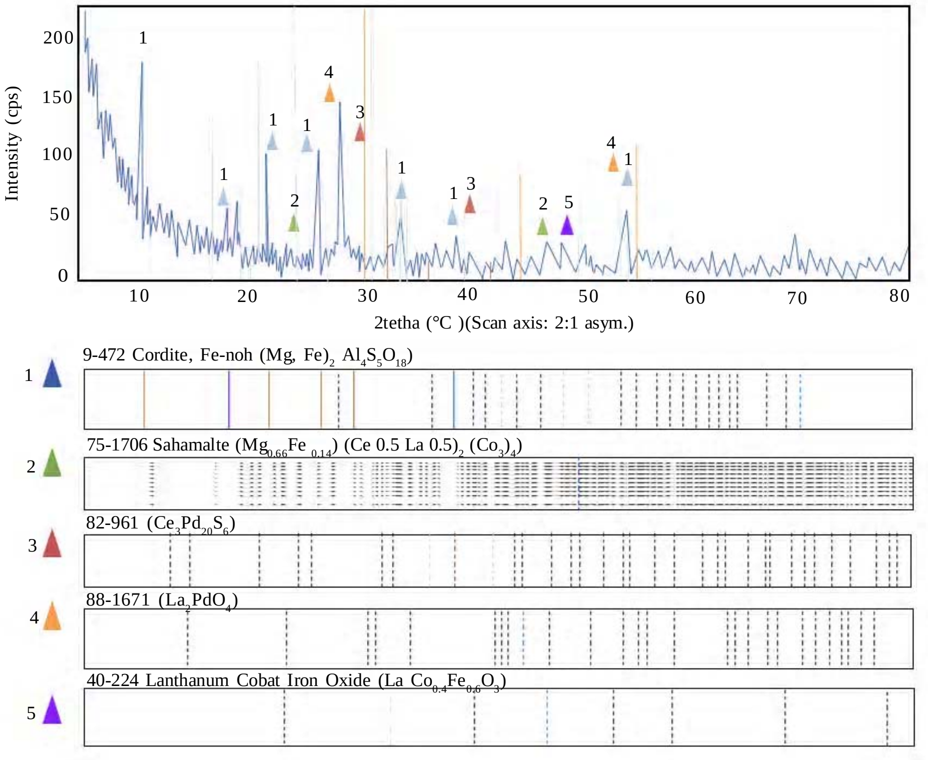

Fig. 1: XRD profiles of prepared catalyst that calcined at 760 °C for 3 h

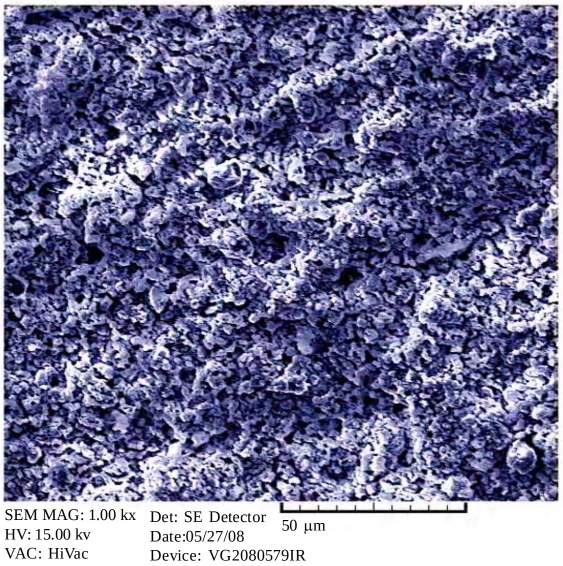

Fig. 2: SEM micrographs of the catalysts prepared by citrate method (La-Ce) (Fe,Co,Pd) O_3 and calcined at 760 °C for 3 h

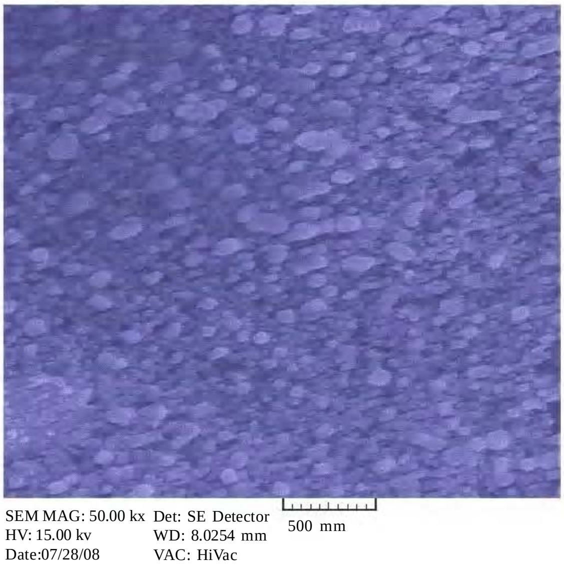

Fig. 3: SEM micrographs of the catalyst coat prepared by citrate method (La-Ce)(Fe,Co,Pd) O_3, calcined at 760 °C for 3 h

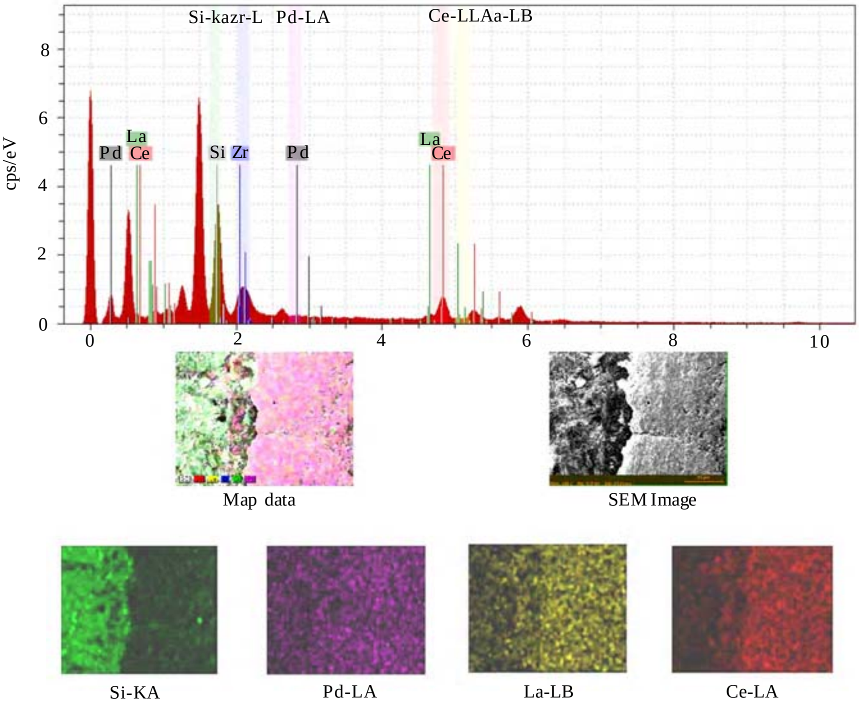

Fig. 4: Map of the coat

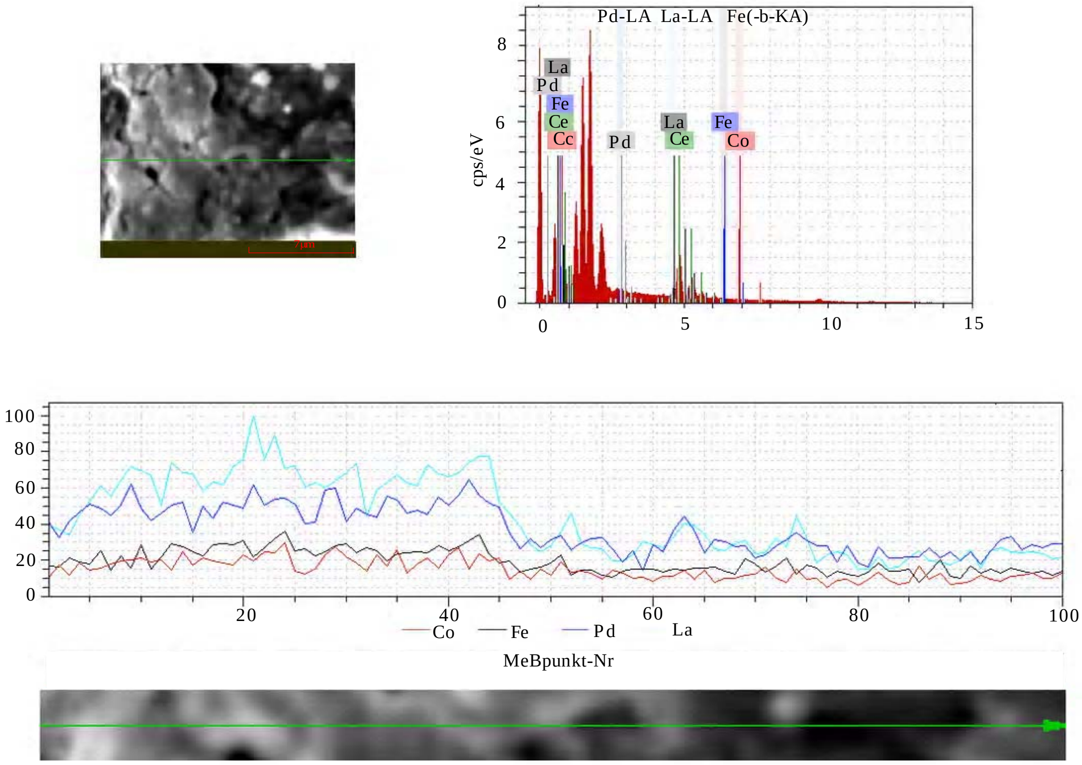

Fig. 5: Line scan of the coat

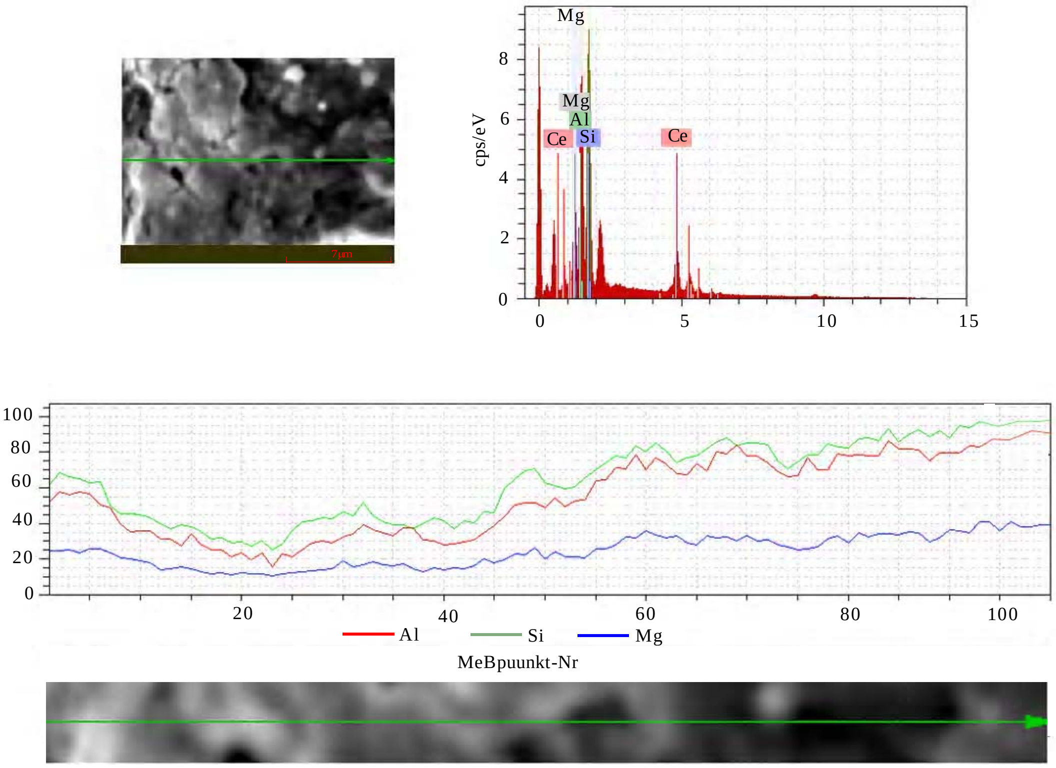

Fig. 6: Line scan of the coat

of (La-Ce)(Fe,Co,Pd)O_3 calcined at 760 °C illustrated the interface between coat and base.

It was clear that there was a strong stick between cordierite base and coat substance. Fluctuations in line scan indicated reactions between coat materials and base.

In accordance with map and line scan, X-ray diffraction shows [((Mg,Fe)$_2$Al$_4$Si$_5$O$_{18}$)],(Ce$_3$Pd$_{20}$Si$_6$) and [((Mg$_{0.86}$Fe$_{0.14}$)(Ce$_{0.5}$La$_{0.5}$)$_2$(CO$_3$)$_4$)] phase between coat materials and base too.

CONCLUSION

The prepared (La-Ce)(Fe,Co,Pd)O_3 samples exhibited good activities as regular noble metal catalysts with the highest conversion.

Pd-based materials are well known highly active catalysts for a wide range of heterogeneous reactions from fine chemical synthesis (Blaser *et al.*, 2001) to partial or full oxidation reactions (Ciuparu *et al.*, 2002; Centi and Mol., 2001; Gelin and Primet, 2002). Partial reduction of the Pd containing catalyst for a proper duration of time significantly enhances the oxidation activity of the catalyst due to segregation of Pd from the perovskite lattice and its dispersion on the catalyst surface as metallic nanoparticles.

The catalyst was applied on Rd cars and the amount of emission was measured with vehicle emission test systems (AVL) at Sapco company and compared by imported catalyst of Iran Khodro. It can be concluded that Perovskite catalyst reduces emission better than imported catalysts of Iran Khodro company with lower emission and price.

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