

Carbon monoxide oxidation on LaCoO₃ perovskite type catalysts prepared by reactive grinding

Patel Femina and Patel Sanjay

Department of Chemical Engineering Institute of Technology, Nirma University, Ahmedabad-382481, INDIA

Available online at: www.isca.in

(Received 4th October 2011, revised 9th January 2012, accepted 25th January 2012)

Abstract

Perovskite oxides are used as promising three way catalysts for the removal of exhaust gases because of their low cost, thermal and mechanical stability at relatively high temperature, great diversity and excellent redox properties. The major traditional drawback of perovskites is the low specific surface area (usually several m²/g) due to their preparation that involves a rather high temperature (often as high as 800^oC) to ensure the formation of the crystalline phase. This suppresses their activity and to some degree limits their application. A new preparation method called reactive grinding was developed for the synthesis of perovskites at room temperature via high-energy ball milling resulting in a relatively high surface area. Perovskite type mixed oxides LaCoO₃ with high specific surface area was prepared by reactive grinding. These catalysts were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) - Energy dispersive X-ray spectroscopy (EDX or EDS) and BET surface analysis. The formation of the perovskite structure has been shown by X-ray diffraction (XRD) for all samples. The catalytic performance of the samples for carbon monoxide was evaluated. LaCoO₃ found significantly more active than a reference sample prepared by conventional synthesis method using amorphous citrate complexes. The activity per unit surface area was found to depend on grinding conditions and calcinations temperature. These enhanced activities are associated with both rather high surface area and high defect density reached by the reactive grinding synthesis method.

Keywords: Catalytic converter, perovskite, automotive emission, catalyst, citric acid method.

Introduction

Environmental, ecological and health concern result in increasing stringent emissions norms of pollutant emission from vehicle engine^{1,2}. These regulations require the need for more active and durable emission control system. A number of alternative technologies like improvement in engine design, fuel pretreatment, use of alternative fuels, fuel additives, exhaust treatment or simply better tuning of the combustion process etc. are being considered to reduce the emission levels of the engine².

Catalytic converters have been proved to be effective in controlling harmful gaseous emissions (Carbon monoxide (CO) to carbon dioxide (CO₂), hydrocarbons (HC) to CO₂ and water vapor (H₂O) and nitrogen oxides (NO_x) to nitrogen (N₂) and oxygen (O₂)) under normal working conditions for a stoichiometric air to fuel ratio³⁻⁶. The technology to convert simultaneously all three pollutants into innocuous materials is referred to as three way catalysis or three way catalytic converters (TWCs)⁷⁻¹⁰. The important role of automotive catalysts in catalytic converter contain precious noble metals palladium (Pd), platinum (Pt) and rhodium (Rh) is widely recognized for the conversion of three pollutant emissions such as CO into CO₂, NO_x to N₂ and HC into CO₂ and H₂O in engine exhaust gases (Car's tail pipe)⁶⁻¹³.

Due to their high activity and thermal stability, much attention has been paid to perovskite-type oxides, of general formula ABO₃ (where A and B are usually rare earth, alkaline earth, alkali and other large ions such as Pb⁺², Bi⁺³ that fits in to the dodecahedral site of the framework (A coordinated by 12 oxygen) and 3d, 4d and 5d transition metal ions which occupy the octahedral sites (surrounded by six oxygen atoms in octahedral coordination) respectively) as catalysts for complete oxidation of CO in substitution of the very active noble metals which are more expensive, volatilization at high operating temperature, sublimation, do not resist to operating temperatures exceeding 850 K, sintering at high temperature and limited resources of noble metal¹³⁻²³.

Due to the great stability of the perovskite framework a large number of metallic cations can occupy the A and the B sites provided that the tolerance factor $t [t = (r_A + r_O) / \sqrt{2(r_B + r_O)}]$ is in the range 0.8–1.0. Perovskite compounds can also tolerate significant partial substitution (A and/or B with metals (A, B correspondingly) of different oxidation states) and non-stoichiometry while still maintaining the perovskite structure. Metal ions having different valence can replace both A and B ions. This may generate a non-integral number of oxygen atoms^{10,19}.

Several methods are used to synthesis perovskites such as co-precipitation, sol-gel, citrate complexation, micro-emulsion etc. which involves high temperatures (because of their preparation method involving a high temperature heating step as high as 800⁰C) to ensure the perovskite crystallization is their poor specific surface areas (usually less than 2 m²/g) severely limiting their practical application due to low catalytic activity per unit mass^{4,8,19-25}.

For example, Co-based perovskite catalysts prepared by the conventional citrate complexation method have a surface area of only 4–7 m²/g after calcination at 600⁰C for 6 h²⁶. The specific surface area observed on perovskites prepared by these methods rarely exceeds 25 m²/g. A new preparation method for perovskite can allow to avoid the thermal treatment and the crystallize to proceed at nearly ambient temperature. This technique uses high energy ball milling (reactive grinding) resulting in relatively high surface area^{4,18,19,25}. Reactive grinding involve the synthesis of materials by high-energy ball milling e.g. planetary mills, vibratory mills, attritors and tumbling ball mills in which elemental blends (or pre-alloyed powders, oxides, nitrides etc.) are milled to achieve alloys or composite materials²⁷.

The interaction between milling balls and powder particles can be characterized by process like cold welding, plastics deformation and further fragmentation of the particles (The processing involves repeated cold welding, fracturing and rewelding of powder particles in a high-energy ball mill). Mechanical impact during the process reduces the precursors crystallite size to nano scale provides a homogeneous mixture and enhances the solid state diffusion. A wide variety of perovskites with a crystallite size down to 10 nm and a surface area varying between 4 and 100 m²/g have been successfully synthesized for catalysis applications. The resulting materials are in the form of porous and highly agglomerated powders having a large amount of grain boundaries. Doping of both grain boundaries and bulk material could be performed during synthesis.

The synthesis is performed in a closed environment without generating any waste²⁸. Reactive grinding can be done easily under solvent-free conditions and rapidly produces large amounts of well-mixed nanocomposites²⁹. Using various grinding additives, high surface (measured after calcinations at 473 K) perovskites such as LaCoO₃ (>100m²/g), LaGaO₃ (98.6 m²/g), LaCo_xIn_{1-x}O₃ (>110 m²/g) or SrCoO₃ (150 m²/g) were prepared. The Quebec firm, Nanox Inc. has installed a demonstration unit of reactive grinding for the production of perovskite with capacity of 15 t/year³⁰.

In this work, perovskite type oxides (LaCoO₃) was prepared by reactive grinding and citrate method. These structures were characterized by X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX or EDS) and BET

surface analysis. The activity of the samples was also evaluated in carbon monoxide oxidation reaction.

Material and Methods

Catalyst preparation Citrate method: The citrate compound was prepared by complexation of the nitrate salts with citric acid. A concentrated solution of the metal nitrates was mixed with an aqueous solution of citric acid by fixing at unity the molar ratio of citric acid to the metal cations. Metal nitrates (La(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O) were first dissolved in distilled water (25 ml). Citric acid (10% excess over the number of ionic equivalents of cations) was separately dissolved in distilled water (25 ml) and added to the precursor solution under vigorous stirring for 15 min. Excess water was evaporated under slow stirring in oil bath at 80 ⁰C until a gel was obtained. The viscous gel was then dried at 100 ⁰C overnight in hot air oven. The obtained spongy material was finely ground and calcined under air atmosphere at 750 ⁰C for 5 h.

Reactive grinding: As starting compounds, lanthanum oxide (La₂O₃) (99.99% pure) and cobalt oxide Co₃O₄ (97.49%) of the analytic grade (AR) were used. LaCoO₃ sample was prepared from simple oxides by using preliminary mechanochemical treatment (MCA) of the stoichiometric mixture of simple oxides with stainless steel balls in the high energy ball mill i.e. planetary ball mill.

The La₂O₃ was first calcined at 873 K (600 ⁰C) for 24 h in order to transform any lanthanum hydroxide to lanthanum oxide. Thus, 10 gm of prepurified lanthanum oxide and 5 gm of cobalt oxide were mixed (La/Co atomic ratio equal to 1) and introduced in a grinding jar of volume 250 cm³ with 10 balls of 19 mm size, 10 balls of 14 mm size and 8 balls of 10 mm size. The jar and the balls are made with stainless steel material. The jar was closed with a thick cover and sealed with O-ring.

The balls and the powder were put inside the grinding jar of planetary ball mill. On another side of the grinding jar balls of the weight equal to the weight of the grinding material and powder in the first grinding jar were added so that the weight is balanced. Although milling proceeds at room temperature, the numerous ball shocks within the jar slightly increases its temperature. Thus the container was fan cooled and its wall temperature is kept below 313 K. The milling atmosphere in the jar could be controlled by replacing the seal by a filter paper ring in order to let some air seep into the jar (oxidizing atmosphere). In the sealed jar the oxygen in the trapped air is rapidly consumed. The milling was carried out for 26 h as per ball mill operating conditions mentioned in table - 1. Prepared precursor was calcined at 600 ⁰C in air atmosphere for 5 h in muffle furnace.

Table – 1
Ball mill operating conditions

Operating conditions	
Material of jar	Stainless steel
Material of ball	Stainless steel
Speed ratio (Sunwheel and jar speed ratio)	1:-2
jar speed (rpm)	300 (Clock wise)
Sunwheel speed(rpm)	150 (Anti clock wise)
Ball diameter (mm)	19 mm (10), 14 mm (10), 10 mm (08)
Mass of powder in jar in (gm)	15

Catalyst characterization X-ray Diffraction: Phase analysis, lattice parameters and particle sizes were determined by X-ray diffraction (XRD) using PW1774 Spinner Diffractometer system XPERT-MPD operated at 40 kV and 30 mA with Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Spectra were recorded with step scans from 2° to 99° in 2θ angle and 1 s for each 0.05° step. Lattice parameters were calculated from the reflections appearing in the $2\theta = 2-99^\circ$ range using the software program. The identification of the crystal phases took place using the JCPDS (Joint committee on Powder diffraction standards) data bank.

Particle sizes (D) were calculated by means of the Scherrer equation $D = K\lambda/\beta\cos \theta$ after Warren's correction for instrumental broadening. K is a constant equal to 0.9, λ the wavelength of the X-ray used, β the effective line width of the observed X-ray reflection calculated by the expression $\beta^2 = B^2 - b^2$ (where B is the full width at half maximum (FWHM), b the instrumental broadening determined through the FWHM of the X-ray reflection at $2\theta \approx 28^\circ$ of crystalline SiO $_2$ with particles larger than 1000 \AA , θ the diffraction angle).

Energy dispersive X-ray spectroscopy (EDX or EDS): Energy Dispersive of X-Ray (EDX) of samples was carried out in JEOL made instrument JEM2100 model which has attached detector OXFORD Instrument INCA X-SIGHT model. EDX was used to investigate the morphology as well as the elemental composition and distribution of all the catalyst compositional analysis.

BET surface area: BET Surface area of the materials were measured by nitrogen adsorption at the liquid nitrogen temperature (-196°C) using a volumetric all glass apparatus.

The specific surface area of the materials calcined at 600°C prepared by reactive grinding and 750°C prepared by citrate method for 5 h was determined from nitrogen adsorption isotherms measured at -196°C using a Micromeritics ASAP 2020 instrument. Samples were degassed at 300°C under vacuum (10^{-3} Pa) until complete removal of humidity (about 3-4 h) prior to adsorption-desorption experiments. Nitrogen

adsorption measurements were performed up to a relative pressure $P/P_0 = 1$. The specific surface area was determined from the linear part of the BET curve. The pore size distribution was calculated from the desorption branch of N $_2$ adsorption/desorption isotherms using the Barrett-Joyner-Halenda (BJH) formula. Pore volume and average diameter were also obtained from the pore size distribution curves using the software.

Catalytic activity: The catalytic oxidation tests were carried out in a stainless steel fixed bed reactor (I.D. 1.805 cm, O.D. 1.905 cm and L.50 cm) equipped with flow controllers and heating system.

Before the activity tests, the catalyst in the bed was activated by passing N $_2$ (86 %) and O $_2$ (14 %) at $490 \text{ N cm}^3 \text{ min}^{-1}$ for 2 h at 500°C below the calcinations temperature to remove adsorbed moisture and cool with passing N $_2$ at $420 \text{ N cm}^3 \text{ min}^{-1}$ till bed temperature reach to 100°C .

CO oxidation tests were carried out in a fixed bed of catalyst particles (ca. 1 g) mixture previously added with 3 g of SiO $_2$ (0.5–1.5 mm granulate) in order to reduce the specific pressure drop across the reactor and to prevent thermal runaways placed between two ceramic blanket wool and inserted into the reactor. The reactor was placed in a tubular PID-regulated oven and the temperature was monitored with a K type thermocouple positioned in correspondence to the catalyst bed. The gaseous flow rates were measured by rotameter and mixed at atmospheric pressure to obtain inlet concentrations of 7.8 % CO, 13 % O $_2$, N $_2$ as balance with a gas hourly space velocity (GHSV) of $32,000 \text{ Ncm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for reactive grinding and 7.9 % CO, 9.64 % O $_2$, N $_2$ as balance with a gas hourly space velocity (GHSV) of $29,000 \text{ Ncm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for citrate method. Reaction temperature was raised from 473 to 873 K and product stream was analyzed by gas chromatography (GC 2010 Model) using Shin Carbon ST micropacked column and μTCD detector. The CO conversion in activity tests was defined as:

$$X_{\text{CO}} = (F_{\text{f,CO}} - F_{\text{p,CO}}) / F_{\text{f,CO}}$$

Where $F_{\text{f,CO}}$: Molar flow rate of CO in feed stream, $F_{\text{p,CO}}$: Molar flow rate of CO in product stream

Results and Discussion

Catalyst characterization: Figure - 1 illustrates X-ray diffraction pattern of LaCoO $_3$ prepared by reactive grinding and citrate method. The comparison of these spectra with JCPDS charts indicates that LaCoO $_3$ sample prepared by reactive grinding is essentially perovskite type mixed oxides (JCPDS card 37-0804). Other phases, such as Co $_3$ O $_4$ (JCPDS card 43-1003) and La(OH) $_3$ (JCPDS card 36-1481) were detected in addition to the major ABO $_3$ perovskite phase.

The comparison of these spectra with JCPDS charts indicates that Co based samples prepared by citrate method is essentially perovskites type mixed oxides (JCPDC card 00-025-1060, 00-006-0491). Phase formation is closely related to the calcination temperature. At 750 °C, the catalyst sample completely transformed lanthanum and cobalt nitrates into LaCoO₃ perovskite phase. No spinel phase La₂CoO₄ (that normally tends to form at higher temperatures) was observed in these sample.

In figure - 1 (a) and (b), the XRD patterns of two LaCoO₃ samples prepared by reactive grinding and citrate method are compared. They show some differences in the intensity of the perovskite peaks at the same angles. This, in fact indicates that citrate method has been more successful in forming perovskite phase with a higher degree of crystallinity. The crystallite sizes of prepared perovskites calculated by Scherrer's equation after Warren's correction of instrumental broadening are also reported in table - 2.

Surface area, pore size and pore volume are among the most fundamentally important properties of a catalyst because they determine the measure of its internal surface available to accommodate active sites for high catalytic activity by providing accessibility of the active sites to reactants and the extent to which transport of products from the catalyst surface to the bulk fluid. The results for the nitrogen isothermal sorption at 77 K for perovskite- type mixed oxides synthesized by reactive grinding after calcinations at 600°C for 5 h and synthesized by citrate method after calcinations at 750 °C for 5 h are presented in figure - 2, respectively. All the isothermal results show hysteresis loops whose characteristics exhibit dependence on the structure of the samples that are confirmed to be with a porous morphology.

The specific surface area (BET surface area), crystallite size, pore size and pore volume of the samples synthesized by reactive grinding after calcinations at 600 °C for 5 h and synthesized by citrate method after calcinations at 750 °C for 5 h are listed in table - 2.

After milling for a certain length of time in reactive grinding, steady-state equilibrium is attained when a balance is

achieved between the rate of welding which tends to increase the average particle size and the rate of fracturing which tends to decrease the average composite particle size. Smaller particles can withstand deformation without fracturing and tend to be welded into larger pieces with an overall tendency to drive both very fine and very large particles toward an intermediate size. Hence, the perovskite samples prepared by reactive grinding after 26 h milling has lower surface areas than the sample prepared by the citrate method due to cold welding become predominate over fracturing which forms agglomerates in reactive grinding after milling of 26 h.

The citrate method has adsorption-desorption isotherms of the catalysts have shown similar characteristics. Barrett-Joyner- Halendar (BJH) analysis showed that catalyst pores were meso size and the average pore sizes were found to be 9.77 nm for citrate method and 16.94 nm for reactive grinding methods respectively.

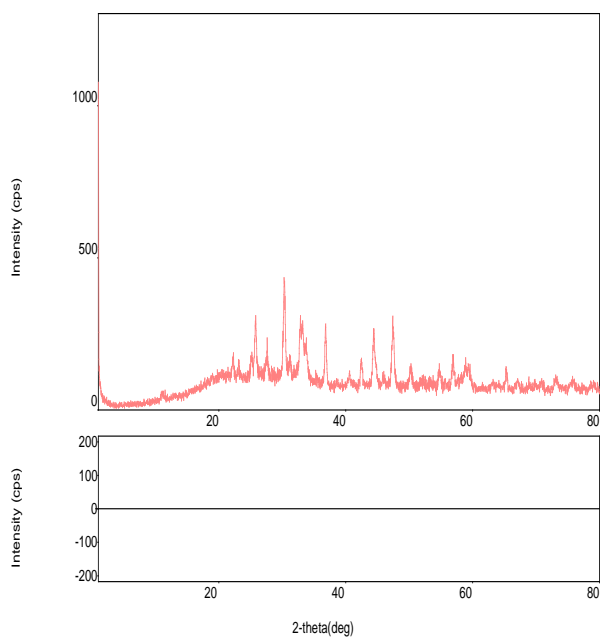
According to semi-quantitative EDX results, table - 3 shows the relative atomic concentrations of La and Co for LaCoO₃ prepared by reactive grinding. The values shown in table - 3 were calculated by the EDX software using an averaged signal from several thousand particles. The compositions of the catalysts intended and the EDX test results seem to be in good agreement.

Catalytic oxidation of CO: The catalytic combustion tests (W/F = 0.124 g/cm³ s⁻¹) were performed with a gas mixture containing over the catalyst samples prepared by the reactive grinding and the citrate method as a function of temperature. Figure - 3 shows the effect of temperature on % CO combustion for the catalyst prepared by reactive grinding and citrate methods respectively. This figure show that those sample exhibit large differences in terms of the catalytic activity with the sample reactive grinding displays the highest activity for CO conversions higher than 90 %. As figure - 3 shows, 94 % CO combustion for this catalyst sample was achieved only at 534 °C. In general, the citrate sample shows lower CO conversion than the reactive grinding at the same temperature.

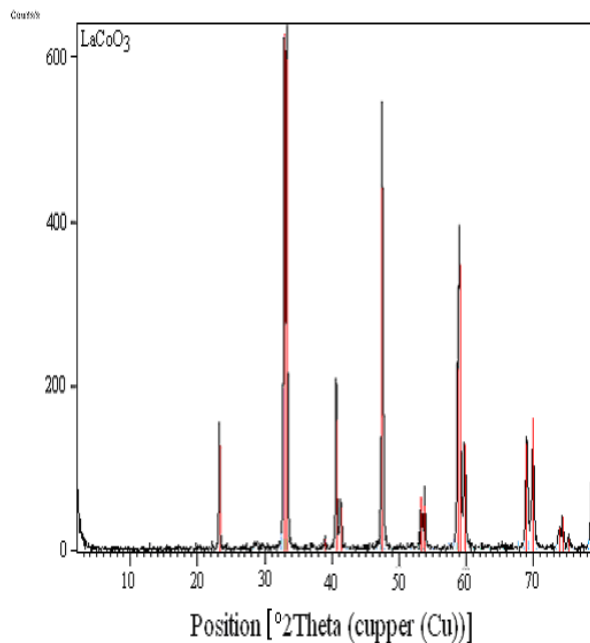
Table - 2
Properties of Co-based catalysts

Sr. NO.	Sample	Calcination T (°C)	Crystallite Size (nm)	Phases	Specific Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)
1	LaCoO ₃ - RG	600	40-48	P+O	6.08	16.94	0.0258
2	LaCoO ₃ - CT	750	35-56	P	8.78	9.77	0.0214

Reactive grinding (RG): P+O: LaCoO₃, CO₃O₄, La(OH)₃ Citrate method (CT): P: LaCoO₃

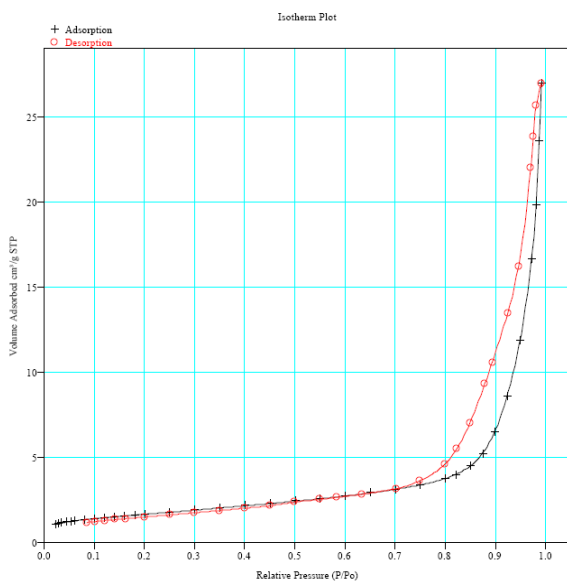


(a)

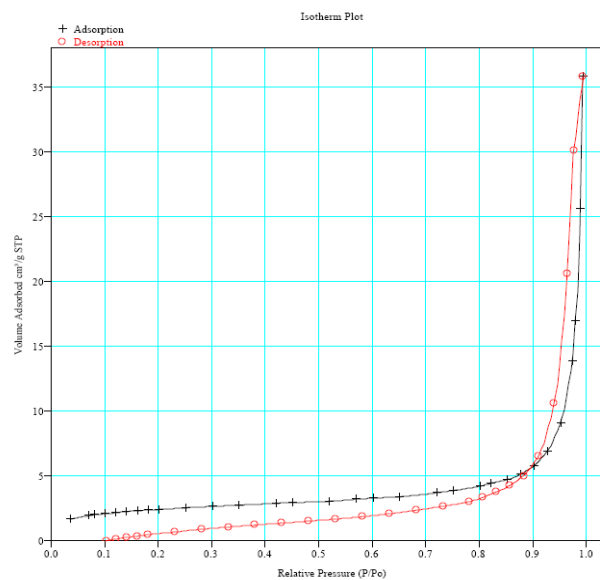


(b)

Figure - 1
XRD patterns of LaCoO₃ (a) prepared by reactive grinding (b) prepared by Citrate method



(a),



(b)

Figure - 2
N₂ adsorption-desorption isotherm of LaCoO₃ (a) prepared by reactive grinding (b) prepared by citrate method

Table - 3
Sample compositions determined by EDX for LaCoO₃ prepared by reactive grinding

Element	Weight %	Atomic %	Weight gm	Weight %	gm atom	Atom ic %
	Experimental		Theoretical			
O	25.32	70.40	2.926	19.50	0.1829	60.02
Co	13.07	9.86	3.598	23.98	0.0609	19.98
La	61.61	19.73	8.476	56.50	0.0609	19.98
Total	100	100	15	100	0.3047	100

The temperature corresponding to 50% conversion of CO is defined as the catalyst “light off” temperature and it is an important parameter in catalytic reactions. The lower the light off temperature, the more active the catalyst is. The light off temperature for a catalyst prepared by reactive grinding is 385 °C for CO oxidation.

The catalytic activity of the perovskite samples chiefly depends on three factors: chemical composition, degree of crystallinity and the crystals morphology (including particle sizes, pore size distribution and specific surface area of the perovskite catalyst). All these factors are affected by the synthesis method and the specific synthesis operating conditions.

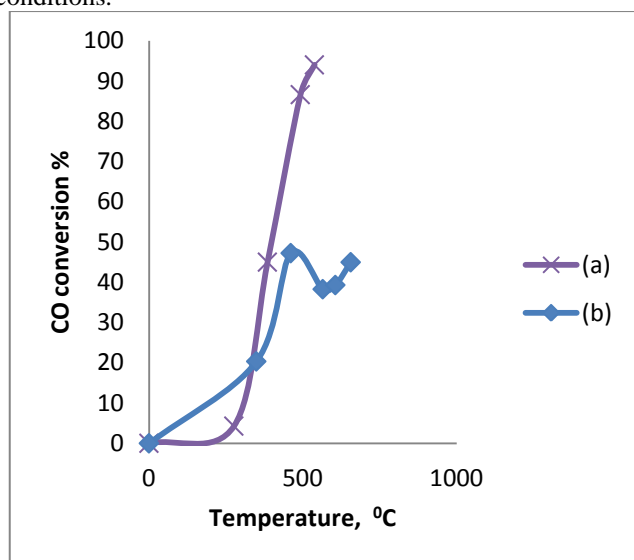


Figure - 3

CO conversion as function of temperature for LaCoO₃ perovskites (a) Prepared by reactive grinding (CO: 7.8 %, O₂: 13 %, N₂: 79 %, SV : 32000 Ncm³g⁻¹h⁻¹) and (b) Prepared by citrate method (CO: 7.9 %, O₂: 9.64 %, N₂: 82.39 %, SV : 29000 Ncm³g⁻¹h⁻¹)

Reactive grinding produces mixed oxides consisting of agglomerates of nanocrystalline domains. Their specific surface area can be increased by partial detachment of the

nanoparticles which yields a looser agglomerates. The resulting solid exhibits nanoparticle properties and these agglomerates is the presence of a high density of nanoscale grain boundaries. As oxygen mobility is usually higher in grain boundaries, their occurrence is especially important for the catalysis of redox reactions. Due to this higher oxygen mobility, LaCOO₃ prepared by reactive grinding displays the highest activity for CO conversions compare to LaCoO₃ prepared by citrate method which has large surface area compare to reactive grinding.

Conclusion

LaCoO₃ Perovskite catalysts were prepared by reactive grinding and citrate method. XRD tests showed the existence of LaCoO₃, Co₃O₄ and La(OH)₃ phases for reactive grinding and pure LaCOO₃ for citrate method. BET surface area measures indicated that LaCOO₃ catalyst prepared by citrate method has the largest surface area than prepared by reactive grinding. Perovskites prepared at room temperature by the reactive grinding technique yields solids which are very active in the catalytic oxidation of carbon monoxide. Compared to classical preparation procedures this increased activity is due to the presence of a high density of nanoscale grain boundaries. As oxygen mobility is usually higher in grain boundaries, their occurrence is especially important for the catalysis of redox reactions. Moreover, because reactive grinding does not involve high temperatures, the solids prepared by this technique have their surfaces essentially covered with OH and therefore the calcination temperature is a factor of their catalytic activity. Activity tests of the catalysts shows that LaCoO₃ has 86 % conversion for CO at 492 °C even it has surface area slight lower than citrate method.

Acknowledgement

The work described above was fully supported by a research grant from the Nirma University.

References

1. Thakur Prabhat Rahul, Mathur Anil and Balomajumder Chandrajit, Biofiltration of volatile organic compounds (VOCs) – An overview, *Research Journal of Chemical Sciences*, **1(8)**, 83-92 (2011)
2. Bera A. and Hegde M.S., Recent advances in auto exhaust catalysis, *Journal of the Indian Institute of Science*, **90(2)**, 299-325 (2010)
3. Shinjoh H., Rare earth metals for automotive exhaust catalysts, *Journal of Alloys and Compounds*, 1061-1064 (2006)
4. Zhang R., Villanueva A., Alamdari H. and Kaliaguine S., Catalytic reduction of NO by propene over LaCO₁.

- $x\text{Cu}_x\text{O}_3$ perovskites synthesized by reactive grinding, *Applied Catalysis B: Environmental*, **64**, 220-233 (2006)
- Mouza A.A., Peolides C.A. and Paras S.V., Utilization of used auto-catalytic converters in small countries: the Greek paradigm, *Resources, Conservation and Recycling*, **15**, 95-110 (1995)
 - Nishita Y., Mizuki J., Tanka H., Uenishi M. and Kimura M., Self-regeneration of palladium-perovskite catalysts in modern automobiles, *Journal of Physics and Chemistry of Solids*, **66**, 274 – 282 (2005)
 - He H., Dai H. and Au C., An investigation on the utilization of perovskite type oxides $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($\text{M}=\text{Co}_{0.77}\text{Bi}_{0.20}\text{Pd}_{0.03}$) as three way catalyst, *Applied Catalysis B: Environmental*, **33**, 65-80 (2001)
 - Giannakas A., Leontiou A., Ladavos A. and Pomonis P., Characterization and catalytic investigation of O+CO reaction on Perovskites of the general formula $\text{La}_x\text{M}_{1-x}\text{FeO}_3$ (M= Sr and/or Ce) prepared via a reverse micelles micro emulsion route, *Applied Catalysis A: General*, **309**, 254-262 (2006)
 - Fabbrini L., Rossetti I. and Forni L., Effect of primer on honeycomb-supported $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$ perovskite for methane catalytic flameless combustion, *Applied Catalysis B: Environmental*, **44**, 107-116 (2003)
 - Screen T., Platinum group metal perovskite catalysts – Preparation and Application, *Platinum Metals Review*, **51**(2), 87–92 (2007)
 - Seyfia B., Baghalhaa M. and Kazemianb H., Modified LaCoO_3 nano-perovskite catalysts for the environmental application of automotive CO oxidation, *Chemical Engineering Journal*, **148**, **306–311** (2009)
 - Nishihata Y., Cleaning up catalyst, News and views, *Nature*, **418**, 138 (2002)
 - Farrauto R. J. and Heck R. M., Catalytic converter: State of the art and perspective, *Catalysis Today*, **51**, 351 - 360 (1999)
 - Belton D.N. and Taylor K.C., Automobile exhaust emission control by catalysts, *Current Opinion in Solid State and Material Science*, **4**, 97-102 (1999)
 - Matsumoto S., Recent advances in automobile exhaust catalyst, *Catalysis Today*, **90**, 183-190 (2004)
 - Twigg M.V., Automotive exhaust emission control, *Platinum Metal Review*, **47** (4), 157-162 (2003)
 - Koltsakis G.C. and Stamatelos A.M., Catalytic automotive exhaust after treatment, *Progress in Energy Combustion Science*, **23**, 1-39 (2007)
 - Singh U., Li J., Bennett J., Rappe A., Seshadri R. and Scott S., A Pd-doped perovskite catalyst, $\text{BaCe}_{1-x}\text{Pd}_x\text{O}_{3-\delta}$ for CO oxidation, *Journal of Catalysis*, **24**, **349-358** (2007)
 - Royer S., Berube F. and Kaliaguine S., Effect of the synthesis conditions on the redox and catalytic properties in oxidation reduction of $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$, *Applied catalysis A: General*, **282**, 273-284 (2005)
 - Alifanti M., Florea M. and Parvulescu V.I., Ceria-based oxides as supports for LaCoO_3 perovskite catalysts for total oxidation of VOC, *Applied Catalysis B: Environmental*, **70**, 400–405 (2007)
 - Luod Y. W. L. and Liu W., Combustion synthesis and characterization of porous perovskite catalysts, *Journal of Chemical Science*, **119** (3), 237–241 (2007)
 - Zhang R., Villanueva A., Alamdari H. and Kaliaguine S., Cu- and Pd-substituted nanoscale Fe-based perovskites for selective catalytic reduction of NO by propene, *Journal of Catalysis*, **237**, 368–380 (2006)
 - Cimino S., Lisi L., Rossi S., Faticanti M. and Porta P., Methane combustion on perovskites-based structured catalysts, *Catalysis Today*, **59**, 19–31 (2000)
 - Ozuomba J.O. and Ekpunobi A.J., Sol-Gel Derived Carbon Electrode for Dye-Sensitized Solar Cells, *Research Journal of Chemical Sciences*, **1**(8), 76-79 (2011)
 - Zhang R., Villanueva A., Alamdari H. and Kaliaguine S., Reduction of NO by CO over nanoscale $\text{LaCO}_{1-x}\text{Cu}_x\text{O}_3$ and $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$, *Journal of Molecular Catalysis A: Chemical*, **258**, 22–34 (2006)
 - Chang Y. and McCarty J., Novel oxygen storage components for advanced catalysts for emission control in natural gas fueled vehicles, *Catalysis Today*, **30**, 163-170 (1996)
 - Chicinas I., Soft magnetic nanocrystalline powders produced by mechanical alloying routes, *Journal of Optoelectronics and Advanced Materials*, **8** (2), 439-448 (2006)
 - Ghasdi M. and Alamdari H., CO sensitive nanocrystalline LaCoO_3 perovskite sensor prepared by high energy ball milling, *Sensors and Actuators B*, **148**, 478–485 (2010)

29. Wang Lu C., Liu Y., Chen M., Cao Y., Yong He, Wu G., Dai W. and Fan K., Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis, *Journal of Catalysis*, **246**, 193–204 (2007)
30. Szabo V., Bassir M., Van Neste A. and Kaliaguine S., Perovskite-type oxides synthesized by reactive grinding Part II: Catalytic properties of $\text{LaCo}_{(1-x)}\text{Fe}_x\text{O}_3$ in VOC oxidation, *Applied Catalysis B: Environmental*, **37**, 175–180 (2002)