Abstract

Air pollution generated from automobiles has been a burning issue because of poisonous gases like carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NOx) and particulate matters (PM) emitted by automobiles. These pollutants create adverse effect on human health, air quality and the environment that lead in stringent regulations in the form of emission norms. To control tail pipe emission from two/four wheelers, three way catalytic converter based on Pt-Pd-Rh have been used successfully however it has some limitations. Perovskite oxides (with general formula ABO3 where A and B are rare earth, alkaline earth, alkali metal and transition metal cations respectively) can be alternative catalytic material to this noble metals based three way catalytic converter for automotive CO oxidation because of their low cost, thermal stability at high temperature, high mechanical stability and excellent redox properties.

Perovskites are mainly prepared by ceramic and wet chemical methods. These methods produce low specific surface area perovskite, they are complicated and relatively expensive to put into practice. To overcome the limitations of above conventional methods used for preparation of perovskites an improved high energy (planetary) ball mill has been designed and developed for reactive grinding. The reactive grinding method using improved planetary ball mill produces perovskites in an efficient, simpler and economical manner. Because of flexibility in varying rotation-to-revolution speed ratio and rotational direction of the jar to the revolution disk, significant large specific impact energy can be imparted which form perovskite phase without heat treatment.

In the present study, perovskite catalysts (LaCoO3, LaMnO3, LaFeO3, LaCo0.8Cu0.2O3, La0.8Sr0.2CoO3, La0.8Sr0.2Co0.8Cu0.2O3, La0.8Ce0.2CoO3 and LaCo0.95Pd0.05O3) were prepared by citrate complexation, co-precipitation and reactive grinding methods. Prepared catalysts were characterized by various characterization techniques such as TG-DTA, XRD, BET, SEM, EDX, TEM, particle size analysis, H2-TPR and O2-TPD. The catalytic performance of the perovskites for automotive CO oxidation was carried out using atmospheric gas-solid fixed bed catalytic reactor with simulated gas mixture containing 1% CO, 1% O2 and balance N2.
The detailed preparation parameters affecting the perovskites prepared in planetary ball mill via reactive grinding was studied. The various parameters like basic disc (sun wheel) direction and revolution speed, grinding jar direction and rotation speed, ball to powder weight ratio, milling time, extent of jar filling and heat treatment were optimized for LaCoO$_3$ perovskite catalyst. The parameters were optimized based on physicochemical properties and the catalytic activity. The optimized operating conditions for reactive grinding method using planetary ball mill are recommended as jar speed: 350 rpm (clockwise), sun wheel speed: 200 rpm (anti-clockwise), ball to powder weight ratio: 15:1, milling time 11 h.

The effect of preparation method on LaCoO$_3$ perovskite catalyst for CO oxidation studied. The performance was almost similar for all perovskites prepared by various methods. LaCoO$_3$ perovskite catalyst prepared by co-precipitation method exhibited marginally higher catalytic activity compared to all catalyst compositions. LaCoO$_3$ perovskite catalyst prepared by reactive grinding method, milled for 11 h without heat treatment exhibited minute lower activity for CO oxidation due to dislodging of iron impurities through MOC of grinding jars and balls which contaminated the catalyst surface. Substitution of 20% Cu in LaCoO$_3$ perovskite catalyst (LaCo$_{0.8}$Cu$_{0.2}$O$_3$) prepared by reactive grinding method, milled for 11 h with heat treatment at 600 ⁰C for 5 h enhanced the catalytic activity for CO oxidation. The enhanced activity of Cu substituted catalyst was due to anion vacancies created after Cu substitution which increased the desorption rate of $\alpha$-O$_2$ at lower temperature. The results of the various characterization techniques were used to relate the observed catalytic activity and stability of the catalysts. H$_2$-TPR and O$_2$-TPD results show that Pd facilitates the reducibility of Co in LaCo$_{0.95}$Pd$_{0.05}$O$_3$ perovskite catalyst prepared by reactive grinding method, milled for 11 h without and with heat treatment at 600 ⁰C for 5 h and enhanced $\alpha$-O$_2$ desorption. Among catalysts prepared by reactive grinding, LaCo$_{0.95}$Pd$_{0.05}$O$_3$ perovskite catalysts show the higher activity for CO oxidation, $T_{50}$ and $T_{100}$ observed at 170 and 240 ⁰C respectively which were lower than that for LaCoO$_3$ perovskite catalyst synthesized by reactive grinding method, milled for 11 h without heat treatment.

The LaCoO$_3$ perovskite catalyst prepared by reactive grinding method, milled for 11 h without heat treatment exhibited 90% CO conversion at temperature 260 ⁰C and high space velocity of 60,000 Ncm$^3$/g h (GHSV). This perovskite catalyst subjected to time-on-stream activity test for 24 h at 300 ⁰C during which it remained stable and exhibited 100% CO conversion. Kinetic study was carried out for CO oxidation over same LaCoO$_3$ perovskite
catalyst prepared by reactive grinding method at following operating conditions: WHSV = 20,000-60,000 Ncm³/g h, temperature = 100-300 °C and feed gas = 1% CO, 1% O₂ and 98% N₂ at atmospheric pressure. CO conversion rate increased with contact-time and temperature. The CO oxidation was a first order reaction with activation energy 11.94 kcal/mol.