EXHAUST GAS CLEANING BY THREE WAY CATALYTIC CONVERTERS

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Abstract
The object of this study is to develop a three way catalytic converter (TWC) for removal of three main exhaust pollutants; hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) which are dangerous for both human health and environment. Previously, we developed Ag and Ce based perovskite type catalysts which are known to be active for methane combustion. We obtained full conversion of methane at 450°C with Ag substituted perovskite catalysts which are also known very active for CO and NOx removal. In our earlier work, catalysts are prepared by sol-gel method and calcined at 973 K for 5 hours. In this study, we plan to apply flame spray pyrolysis method to produce the particles as well. Catalyst will be characterized by SEM-EDS, XRD and BET surface area to describe physical properties of the both powder and monolith coated catalysts. The activity measurements of the catalysts are planned based on the real engine emission gas mixture. 0.5 % C_3H_8, 1.5 % CO, 0.4 % NO and 14 % CO_2 balance with N_2 will be tested under fuel lean and rich conditions. Activity tests will be carried out for both in powder form and monolith coated catalysts. 0.2 mg powder catalysts will be placed in a 0.6 cm outer diameter quartz tubular reactor and the three main pollutants HC, NO, CO concentrations in the outlet gas stream will be analyzed with online HC, CO and NOx gas monitors. The same catalyst will be coated on 2 cm diameter 400 cpsi cordierite monoliths and activity tests will be carried out in a stainless steel reactor.
Keyword: *emissions, gas cleaning, catalyst, TWC*

Introduction

By the early 1970s increased use of cars around the world had resulted in serious concerns due to engine exhaust gas emissions. Today, air quality is a big concern and environmental regulations on exhaust pollutants are now stricter than ever. There are many studies to decrease engine emissions by engine and fuel modifications. But these are not the only and sufficient way to decrease emissions. Catalytic emission control is a new and most attractive way to reduce emissions by converting unburned hydrocarbons (HC), carbon monoxide (CO) and Nitrogen oxides (NOx) to partially harmless CO_2, N_2, and water by simultaneous catalytic oxidation and reduction by use of a three way catalytic converter [1,2].

Since 1993, all the gasoline cars are equipped with a three way catalytic converter [3]. Catalyst is referred as the heart of catalytic converter since it is responsible for treating the harmful gases. Although noble metal based (Rh, Pt, Pd) catalyst are the main ones, limited sources, high cost, thermal stability and poisoning problems prompted investigations to find alternative catalysts [2,4].

The alternative catalysts are generally mixed metal oxides, zeolites and perovskites. Perovskite catalysts receive a lot of attention, since they are thermally more stable, better resistant to Pb/S poisoning, less effected by air/fuel ratio and cheaper. Many research focused on them both for automotive exhaust control and catalytic combustion of methane [5].

Perovskites are mixed metal oxides of general formula $ABO_{3\pm\delta}$ where A is usually a lanthanide ion with 12 coordination to oxygen atoms and B is a transition metal ion with 6 coordination to oxygen atoms. Both A and B can be partially substituted, leading to a wide variety of mixed oxides of general formula $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$, characterized by structural and electronic defects, owing to their non-stoichiometry, indicated by the δ subscript in the formula [6,7]. Previously, we oxidized methane which is known as the most stable hydrocarbon. It was fully oxidized at 450 °C with a catalyst composition of $La_{0.7}Ag_{0.3}MnO_3$. Literature shows that, Ag substituted perovskite catalyst is very active on CO and NOx oxidation as well [8,9]. In this study we design Ag substituted TWCs with different composition and coat the catalyst on the cordierite monolithic surface as it is used in real cars.

Experimental Catalyst Preparation Powder catalyst

Catalyst are used both in powder and coated form. Therefore, the first part involves preparing powder catalyst by sol-gel or flame pyrolysis method which is described below.In sol-gel method, appropriate amount of nitrate precursors of catalyst are dissolved in distilled water. Excess amount of citric acid is used as gelling agent. After mixing, resulting solution pH is adjusted with $(NH_4)_2CO_3$. Then vacuum evaporation is applied and the gel

obtained is kept at 393 K in an oven overnight. The resulted solid is calcined at 973 K for 5 hours in high temperature furnace.

Flame synthesis, especially flame spray pyrolysis (FSP), is a relatively new process for one-step synthesis of catalysts. Currently, commercial nanoparticles such as fumed silica, titania, and carbon black in large quantities at low cost are made by the flame synthesis method. Catalysts synthesized by this method have been employed in various catalytic reactions on the laboratory scale, and they showed improved catalytic performances. Their differences in catalytic behaviors are suggested to be due to the structural differences of the flame-made and the conventionally prepared catalysts. We designed a flame spray pyrolysis reactor for a different project to produce nanosize particles.

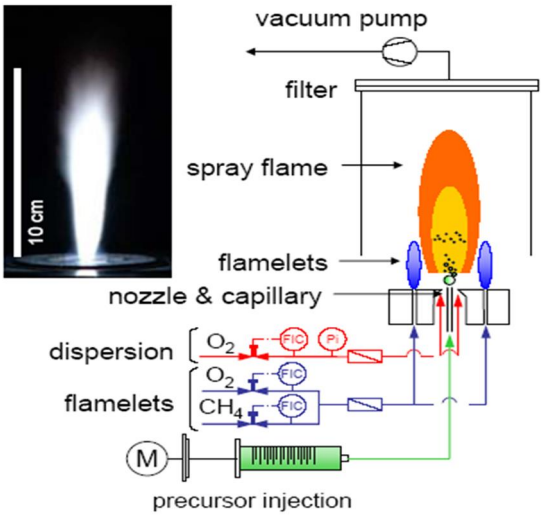

Fig. 1: Flame spray pyrolysis set-up [10]

In this system, precursor solution is fed to a methane flame reactor by a nozzle and particles formed in the flame are collected with a vacuum applied collecter system.

Coating Monolith

Catalyst are coated on 400 cpsi cordierite monoliths having a diameter of 2 cm. Before active phase (perovskite) coating, monoliths are washcoated by ɔ-Al_2O_3 by dip coating technique to increase the surface area. After several dipping steps, washcoated monoliths are coated with perovskite phase. Appropriate amount of perovskite powders are suspended in a diluted acid solution and alumina washcoated cordierite is dipped in this solution several times. After this, monoliths are calcined at 973 K for 5 hours in high temperature furnace.

Catalyst Characterizations

The surface characterizations of the catalyst for both powder and monolithic forms will be measured by SEM-EDS, XRD and BET surface area and the washcoat, active phase distribution, coating thickness, surface porosity and crystal phases will be determined.

Activity Tests

Activity tests will be carried out for both powder (prepared by sol-gel method) and monolithic forms of the catalyst. For powder catalyst 0.2 g catalyst is kept in a quartz flow reactor which has a 0.6 cm outer diameter. The gas mixture composition chosen to test the activity is 0.5% C_3H_8, 0.4% NO, 1.5% CO and 14% CO_2 with balance N_2. According to different driving conditions, activity tests will be carried out with for both fuel rich and lean conditions. Gas hourly space velocities in the activity tests are chosen to be between 30,000h^{-1} and 100,000 h^{-1}. CO, CO_2, HC, NO, O_2 and H_2O species in the outlet gas stream are quantified by online gas analyzers. (Teledyne Model 4020 HC Analyzer, 9110EH NOx Analyzer and 7600 Combined Gas Analyzers). Same procedure is carried out with active phase coated monoliths. The tests is carried out in a stainless steel reactor (2.2 cm OD).

CONCLUSIONS

We have preliminary results obtained based on the previous studies we had and plan to expand our application to exhaust gas cleaning. So far, we obtained full HC conversion at 450^{O}C.

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