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Research Article

Comparative Analysis of NOx Emission Reduction in Engines Using $NiCo_2O_4$ Nanoparticles without External Reductant at Low Temperatures: An Experimental Investigation

C. G. Aswin,[1] A. Kumareswaran,[1] R. Lakshmanan,[1] S. Mathavan,[1] V. Andal,[2] R. Lakshmipathy,[2] and Ivan Leandro Rodriguez Rico[3]

[1]*Department of Automobile Engineering, KCG College of Technology, Chennai 600 100, India*
[2]*Department of Chemistry, KCG College of Technology, Chennai 600 100, India*
[3]*Faculty of Chemical and Pharmacy, Department of Chemical Engineering, Central University "Marta Abreu" of Las Villas, Cuba*

Correspondence should be addressed to V. Andal; andal.che@kcgcollege.com
and Ivan Leandro Rodriguez Rico; ivanl@uclv.edu.cu

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Due to increasingly stringent rules, eliminating pollutants (NOx) emitted by diesel engines in the automobile sector remains an intriguing scientific and technological problem. To meet the strict NOx emission restrictions, a catalytic system with a high level of complexity, unit size, and quantity, as well as higher fuel consumption, is required. As a result, for a reduction in individual exhaust gas emissions, an after-treatment system for a diesel vehicle must employ integrated catalyst technology. For selective catalytic reduction of NOx without any external reductant, a highly effective catalyst "spinel nickel cobaltite" ($NiCo_2O_4$) was produced using a polymeric precursor technique. In this work, an exhaust gas treatment system without external reductants using nano-$NiCo_2O_4$ as catalyst was designed and fabricated, for NOx control in diesel and petrol engines at low temperature. In order to determine the NOx conversion efficiency in the selective catalytic reduction system, tests were carried out at different engine loads. The system was supposed to be cost-effective due to the nano-$NiCo_2O_4$ catalyst's ability to work at low temperatures. The findings proved the developed SCR system's potential to reduce NOx emissions. At a high load, the nitric oxide (NO) emissions were reduced by 54 and 96 percent, respectively, without increasing HC, CO, and CO_2 emissions or compromising efficiency.

1. Introduction

NO_x emissions (NO and NO_2) are a significant source of pollution in the atmosphere. They have a wide range of negative consequences for the environment and human health. The main effects of NO_x on the environment include acidification of rain, photochemical smog, greenhouse effect, and ozone depletion, while the most severe effect of NO_x on people's health is respiratory tract disorders [1–3]. Although many sources such as agriculture, thermal plants, and industry have been considered as contributors to NO_x emissions, the transport sector especially diesel-powered vehicles are the main contributor of NO_x emissions. NO_X is principally produced by a high-temperature endothermic reaction between nitrogen and oxygen in the fuel-air mixture.

Around 40% of total NO_x emissions come from road transport, while diesel-powered cars account for 85% of NO_x emissions from the transportation sector. The challenge for vehicle makers and researchers has been to minimize NO_x emissions from diesel engines without sacrificing engine performance.

To obtain optimal conversion rates in NO_x emissions, numerous research and technological advancements have been done [4]. Pretreatment methods reduce NOx emissions before they are sent to the engine's exhaust port, whereas after-treatment methods reduce NOx emissions after they

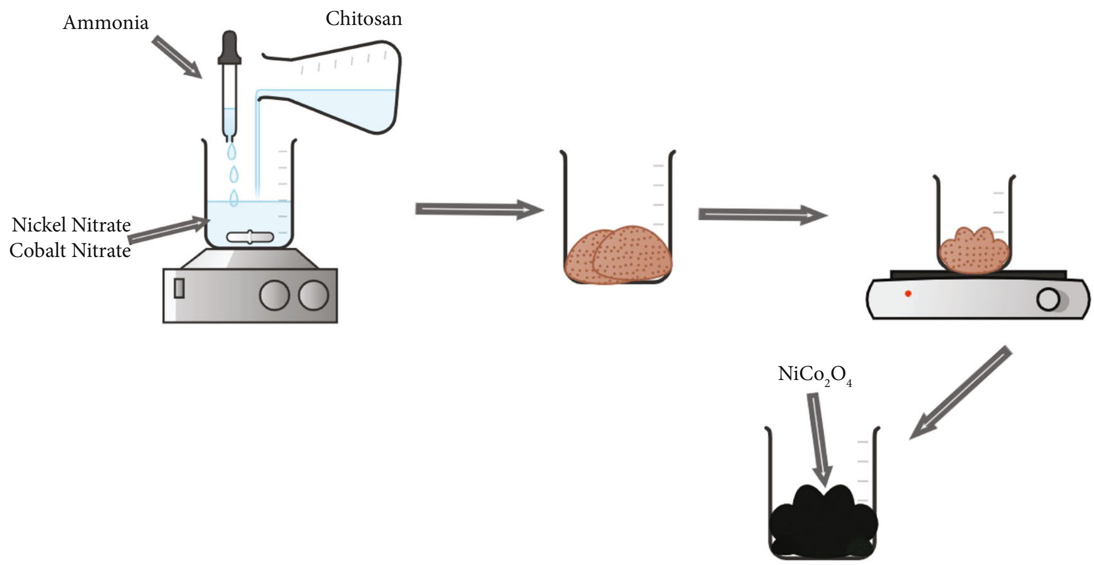

Figure 1: Schematic representation of the synthesis of $NiCo_2O_4$ nanoparticle.

have been directed to the engine's exhaust port. Pretreatment methods for decreasing NOx emissions include exhaust gas recirculation (EGR), electronically controlled fuel injection, engine modification, increased injection time, water spray in the combustion chamber, improved fuel characteristics, and the use of fuel additives. After-treatment technologies including the use of lean NOx trap (LNT) catalysts and the selective catalytic reduction (SCR) systems, which were developed to reduce NOx emissions and are widely used in diesel engines, are the subject of this research [5].

SCR (selective catalytic reduction) of NO_x emissions is a common technique nowadays. With a reductant and catalyst in an SCR system, NO_x emissions from diesel engines can be reduced significantly [6]. The most common reductant and catalyst used to reduce NO_x emissions at high exhaust gas temperatures are ammonia (NH_3) and V_2O_5–WO_3/TiO_2. However, conversion efficiency remains low at low exhaust gas temperatures below 250°C, and NH_3 builds up on the exhaust line and catalyst surfaces. This phenomenon, known as NH_3 slip, has a significant detrimental impact on SCR conversion efficiency and can lead to catalyst degradation [7].

Many catalysts, such as Cu zeolites or Mn oxides, have been created with superior low-temperature SCR activity; however, they are all ineffective in most off-gas circumstances because the active sites are substantially destroyed by sulfur dioxide poisoning [8, 9]. Yu et al. created a Cu-SSZ-13 zeolite-metal oxide hybrid catalyst that has improved SO_2 tolerance by preferring producing Zn sulfate over Cu sulfate [10]. Unfortunately, commercialization in the field is problematic due to the sophisticated catalyst preparation procedure and the requirement for a very high temperature (650°C) to regenerate inactive catalysts [11].

For SCR NOx reduction, a variety of catalysts have been studied, including platinum group metals (PGM), perovskite-type oxides, spinel-type oxides, and mixed transition metal oxides [12–15]. In a low-temperature selective catalytic reduction, low-cost spinels were used [16].

However, in this work, the catalyst used is capable of reducing NOx at low temperatures less than reported temperature of ABS [17] without any external reductant. Further, $NiCo_2O_4$ was chosen as the preferable catalyst in this investigation because of its high activity at low exhaust temperatures, environmental benefits when compared to conventional catalyst toxic effects, and great performance in NOx reduction [18, 19]. NOx conversion efficiency was studied using $NiCO_2O_4$ as a catalyst at two different engines with various loading conditions. Furthermore, using a basic physical mixing strategy is a cost-effective and practical option that can be quickly implemented in the industry. This catalyst reduces additional fuel expenses and carbon dioxide emissions by operating at low temperatures without the use of an external reductant. As a result, it provides enormous economic and environmental benefits.

2. Materials and Methods

2.1. Synthesis of Nano-$NiCo_2O_4$. The polymeric precursor technique [20] was used to make $NiCo_2O4$. The starting components, nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), and chitosan, were employed exactly as purchased. 14.5 g cobalt nitrate and 7 g nickel nitrate were dissolved in distilled water and stirred continuously for 20 minutes. Then, 5% of the chitosan solution was added, and the mixture was stirred constantly at 80°C until it formed a gel, which was then heated at 80°C for 4 hours at a rate of 5°C/min to generate a black powder. The black powder was pounded in an agate mortar and then calcined for 6 hours in an air environment at 300, 500, 700, and 900°C. The schematic representation of synthesis of nano-$NiCo_2O_4$ is shown in Figure 1.

2.2. Engine. The process begins by choosing the engine. Here, a twin-cylinder diesel engine, three-cylinder petrol engine, is used for testing the emission. The twin-cylinder diesel engine

Figure 2: Fabrication of SCR catalytic converter.

Figure 3: Experimental setup of diesel and petrol engine with fabricated SCR.

Table 1: Specifications of engines.

Specification	Diesel engine	Petrol engine
Make	Comet	Maruti-Suzuki S-presso
Cylinder	Two cylinders	Three cylinders
Fuel type	Diesel	Petrol
Engine cubic capacity	1107 cc	999 cc
Cooling agent	Water-cooled	Water-cooled
Speed	1500 RPM	5500 RPM

is a stationary engine with constant speed at different load conditions. The various emissions like HC, CO, NOx, CO_2, and O_2 are noted down at different load conditions.

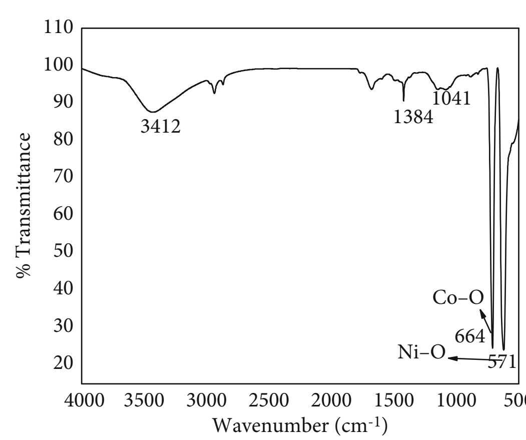

Figure 4: FTIR spectra obtained for $NiCo_2O_4$ nanoparticle.

2.3. Fabrication of SCR System. The honeycomb structure is brought in and the synthesized catalyst (nickel cobalt oxide ($NiCo_2O_4$)) is coated into it using a binder solution of polyvinyl alcohol (PVA). The honeycomb structure is then welded around the edges of a cylindrical metal (Figure 2).

2.4. Experimental Setup. Figure 3 shows a schematic illustration of the experimental setup used to determine the effectiveness of NOx conversion utilizing fabricated SCR systems. A specially designed exhaust system and a generator motor that can be operated at various loads makes up

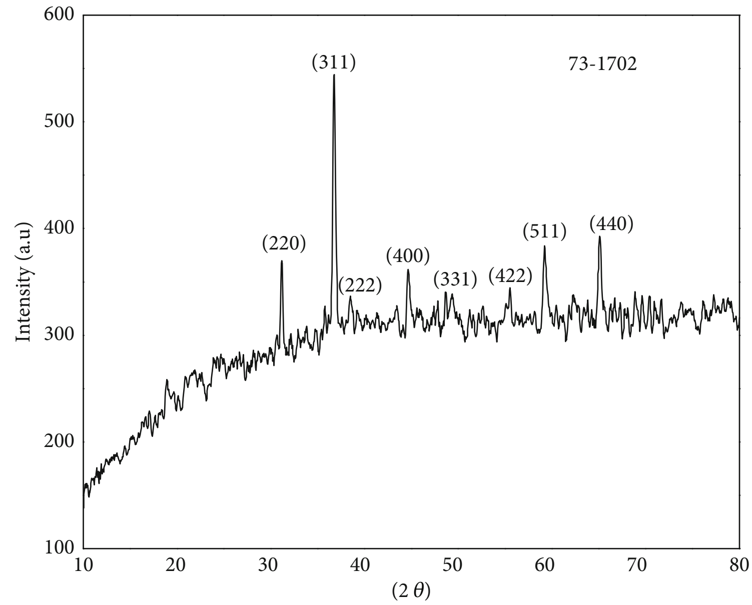

FIGURE 5: XRD pattern of $NiCo_2O_4$ nanoparticle.

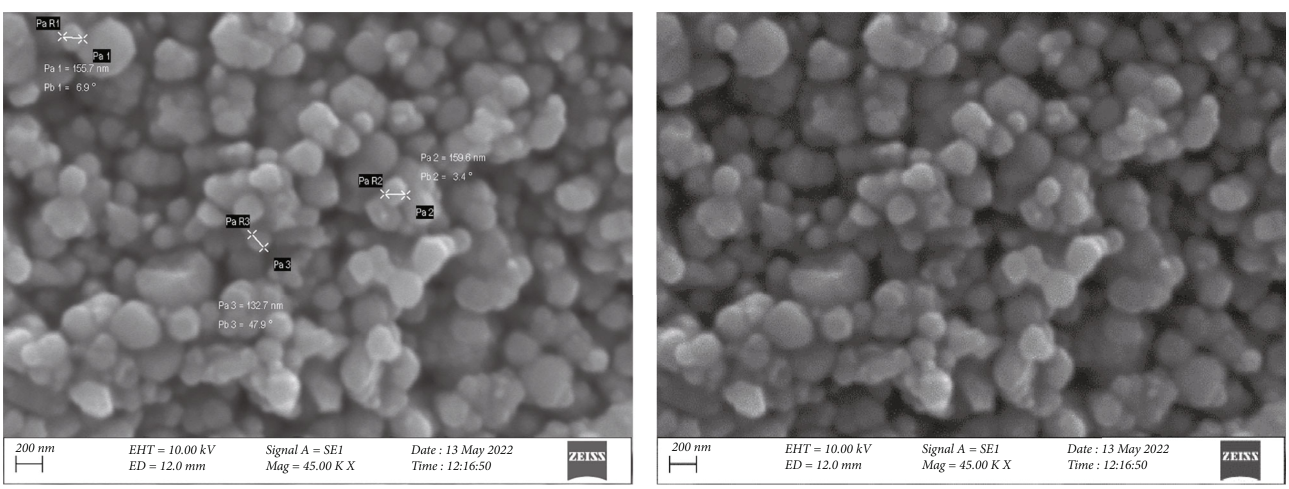

FIGURE 6: SEM images of $NiCo_2O_4$.

TABLE 2: Diesel engine reading without using SCR catalyst.

Load	Without SCR catalyst				
	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO2 (ppm)
0	94	160	11	0.03	1.63
4	116	287	5	0.02	3.05
8	133	351	5	0.01	2.63
12	144	441	11	0.02	2.71

TABLE 3: Diesel engine reading using $NiCo_2O_4$ SCR catalyst.

Load	With $NiCo_2O_4$ SCR catalyst				
	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	99	98	5	0	1.15
4	122	184	4	0.01	1.68
8	142	189	4	0.01	1.51
12	152	200	1	0.01	1.28

the test setup. Experiments were carried out at different engine loads (0 kW, 4 kW, 8 kW, and 12 kW, using two different engines). We chose a twin-cylinder diesel engine and s-presso three-cylinder petrol engine to test the fabricated SCR system with a speed rate of 1500 rpm. The specifications of the engines are given in Table 1. NOx conversion ratios were determined in the tests to determine the performance of the catalyst generated at low exhaust gas temperatures.

2.5. Characterization. X-ray diffraction (XRD) was used to determine the crystalline structure and phase purity of the products using an X-ray diffractometer (Bruker Instrument

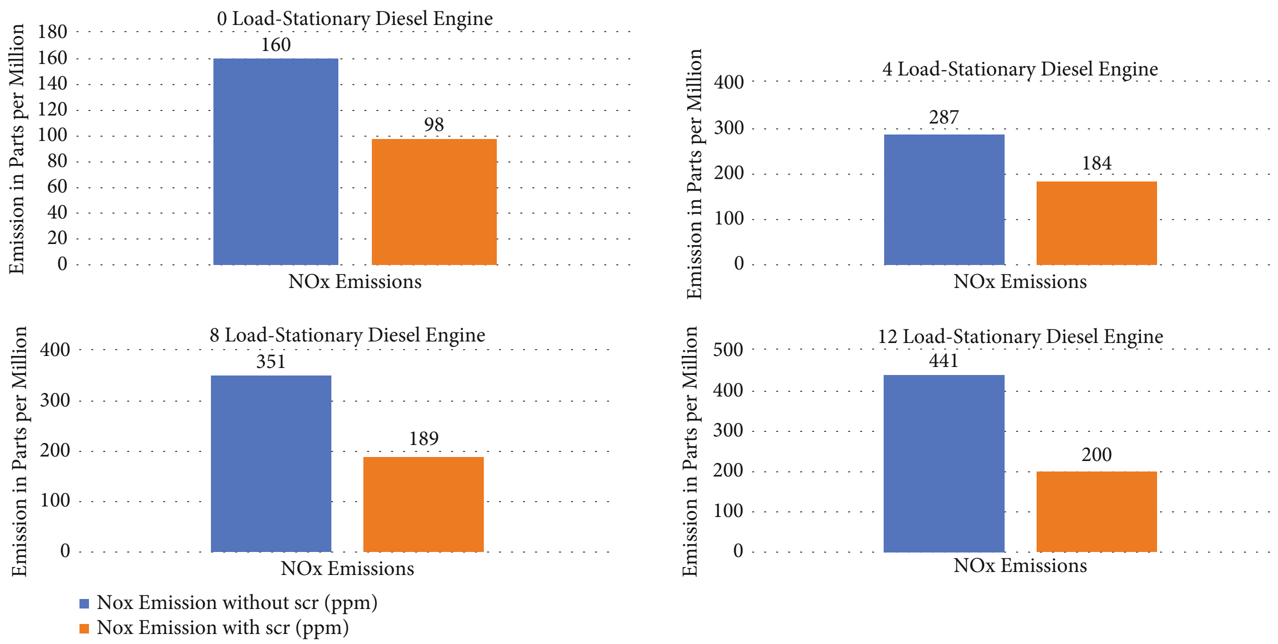

Figure 7: NOx reduction on various loads with and without $NiCo_2O_4$ catalyst in diesel engine.

(D8 Advance)) with Cu-Kα ($\lambda = 1.5418\,\mathring{A}$) radiation ranging from 10 to 80° at ambient temperature. The sample's formation and morphology were studied using scanning electron microscopy (SEM) (FEI QUANTA FEG 200 HR) and Fourier transform infrared spectroscopy (FTIR spectrometer, JASSCO Model 4100). The fabricated catalytic converter is put through its paces with different loads on an emission analyzer. The base readings and the final readings are made as a graph, and from the graph, we can identify the NOx reduction percentage and reduction of other emissions.

3. Results and Discussion

3.1. Characterization of $NiCo_2O_4$. The synthesized $NiCo_2O_4$ sample's FTIR spectrum is shown in Figure 4. The spectrum of $NiCo_2O_4$ spinel exhibits two separate sharp bands in the region of 550 to 650 cm^{-1}, as indicated in the previously published literature. The presence of a metal–oxygen bond in a metal oxide spinel is shown by these two bands. The stretching vibrations of Ni–O bond were assigned to the band at 571 cm^{-1}, while the stretching vibrations of Co–O bond were attributed to the band at 664 cm^{-1} in $NiCo_2O_4$ spinel [21–23].

The XRD spectrum of the as-synthesized $NiCo_2O_4$ nanoparticle is shown in Figure 5. The synthesized sample's XRD pattern is indexed to spinel $NiCo_2O_4$ (JCPDS card no. 73-1702). No other peaks corresponding to NiO or CoO was found which indicates the formation of pure phase $NiCo_2O_4$ [24].

The surface morphology of synthesized $NiCo_2O_4$ nanostructures was examined using SEM. The SEM image in Figure 6 clearly shows the formation of hexagonal-shaped nanostructures of $NiCo_2O_4$ [25].

3.2. NOx Reduction Analysis. The NOx emissions acquired from two different types of engines at different engine loads are illustrated below. The temperature of combustion has a big impact on nitrogen oxide production. At high engine load and high combustion temperature, the highest production of NOx occurs [26–28]. When the engine is under maximum load, high combustion temperatures are reached. High engine load produces more NOx than low engine load. The temperature is the key factor for the highest NOx reduction at higher loads.

In the case of a twin-cylinder diesel engine, the engine rpm was fixed as 1500 rpm but its load is varied from 0 to 12 kW. NOx emissions before and after the SCR catalyst are shown in Tables 2 and 3. There is a considerable reduction in NOx after treatment with $NiCO_2O_4$-modified SCR without an external reductant. On varying load conditions, the catalyst $NiCo_2O_4$ showed superior NOx conversion at all loads, particularly at 12 kW load conditions. Similarly, the overall conversion percentages of HC, CO, and CO_2 were affected by the load. If the temperature of the SCR catalytic converter is between 120°C and 200°C, the most efficient NOx reduction is achieved. The reason for the NOx reduction at low temperature is due to synthesized nano-nickel cobaltite which possesses higher oxygen vacancies in the surface-active site of the catalyst $NiCo_2O_4$. As reported by Trivedi, our catalyst showed good redox property in reducing the NOx at low temperatures due to the surface-active sites [18]. Figure 7 clearly depicts the reduction in NOx with and without SCR catalyst on varying loads.

Similar reports are observed (Tables 4 and 5) when the same SCR catalyst was examined in petrol engine. The efficiency of the SCR catalyst (synthesized nickel cobaltite) was studied using s-presso GDI petrol engine. The engine was run with 1500 rpm speed, but the load is varied from 0 to 16 kg. On varying the load, the NOx reduction occurs maximum at lower temperature from 250 to 320°C. Similar to diesel engine study, HC, CO, and CO_2 also reduced drastically. This further confirms that the catalyst $NiCo_2O_4$

Table 4: Petrol engine reading without using SCR catalyst.

Without SCR catalyst					
Load (kg)	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	253	1	5	0.04	13.52
4	296	2	5	0.15	14.01
8	333	5	36	0.15	14.05
12	354	13	25	0.13	14.07
16	430	25	12	0.32	14.39

Table 5: Petrol engine reading with using SCR catalyst.

With SCR catalyst					
Load (kg)	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	240	0	5	0	0.55
4	258	1	5	0	1.03
8	278	1	5	0	1.89
12	301	2	5	0	2.31
16	322	1	5	0.01	4.58

(nickel cobaltite) has surface-active sites which is more effective in reducing NOx at low temperatures.

Since NOx is a key pollutant for many environmental issues, even though other pollutants are also significantly reduced in both engines, our focus is on NOx reduction. The catalyst's ability to reduce NOx without H_2 may be caused by redox couples of $Ni^{3+/}Ni^{2+}$ (0.58 V/0.49 V) and Co^{3+}/Co^{2+} (0.53 V/0.51 V) as well as oxygen vacancy-rich $NiCo_2O_4$ nanoparticles, which boost the catalyst's reactivity and number of active sites [29].

4. Conclusion

The spinel catalyst $NiCo_2O_4$ was successfully synthesized and fabricated on alumina monolith for NOx reduction study. Two types of engines have been selected, and NOx reduction efficiency was investigated. In the studies, no external reductant was added but the reduction was maximum at lower temperatures. This may be due to the surface-active centers of nanospinel $NiCo_2O_4$ and its morphology. After further investigations over lengthy periods of time on stream from CNG cars, such as water vapors and S-based chemicals, the spinel catalyst $NiCo_2O_4$, which is affordable, highly active, and thermally stable, may be suggested for use as a noble metal alternative in emission management.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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