

Exhaust Gases Pollution Control Using of Bimetallic Nanoparticles and Bimetallic Nanocomposites in Catalytic Converter: A Review

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Abstract— The automotive and chemical reactor application is one of the engineering technologies that can be used to reduce air pollution is the use of catalytic converter mounted on gas exhaust duct. Catalytic converters are employed for reduction and oxidation of toxic gases by-products produced during the burning of fuels. Unfortunately, these tools are very expensive, because the catalyst was made from expensive metals and rarely available such as Palladium, Platinum and Rhodium. Besides, the catalyst is susceptible to fuel with low levels of lead which results in the loss of the function of the catalyst due to blockage in the basic structure of Catalytic Converter. Therefore research needs to be done in the to test the other substrate materials as a catalyst, to study the ability of the catalyst in a catalytic converter to reduce exhaust emissions of Carbon Monoxide and Hydrocarbon. This research is focusses on the history of development of the catalytic converter and the modifications taken place during the recent past years. This paper also shows the study of various bimetallic nanoparticles and bimetallic nanocomposites as a catalyst and there performance capabilities such a way to obtain the suitable Catalytic Converter.

Keywords— Catalytic converter, catalyst, bimetallic nanoparticles, bimetallic nanocomposites.

I. INTRODUCTION

Each and Every industrial Nation is struggling to achieve the strict pollution norms for environment and safety. It has propelled the need to develop a simulated model of catalytic converter before being put in to action. In automobile vehicle exhaust systems, catalytic converters are widely used to reduce unwanted emissions from internal combustion engines. Catalytic converters are also used on many engine-equipped machines including generator sets, forklifts, mining equipment, trucks, busses, trains, etc., to treat the engine exhaust from engines of these machines to reduce pollutants in the exhaust.

The catalytic converter remains the main pollution control device for modern automobiles and chemical reactor application towards reaching the ever-increasing legislative demands for low emission standards. The catalytic converter is expected to attain conversion efficiencies of the order of 90% or above for the main exhaust gas pollutants, like carbon mono oxide, hydrocarbons and NOx. The conversion efficiency is a function of numerous design and operating parameters of the complete system, comprising the system, the exhaust line and the catalytic converter. The design optimization task is especially demanding due to the highly unsteady conditions in the exhaust regarding temperature, flow rate and exhaust composition [1].

A catalytic converter provides an environment for supporting a chemical reaction, wherein unwanted gaseous combustion by-products from an internal combustion engine are converted to more inert gases, which are generally discharged into the atmosphere outside of the vehicle.

The high temperature allows a chemical reaction within the monolith to occur. Ideally, all harmful gasses are converted to safer byproducts such as nitrogen gas, carbon

dioxide, water, etc. However, when engine exhaust contains excessive amount of unwanted contaminants including high levels of nitrous oxides (NO_x), carbon oxides (CO_x) and unburned hydrocarbons (HC), conventional catalytic converters may not be able to effectively treat such an excessive amount of unwanted contamination. In such cases, it may be desired to use some catalyst which help to increase the area of contact and increase the time of reaction inside the catalytic converter [2].

II. USE OF NANO-PARTICLE AS CATALYSTS

A. Nanoparticles

Nanoparticles (NPs) are the nanometer-sized solid particles engineered at atomic or molecular scale so to form either novel or superior physical properties that are not attainable by conventional bulk solids. These man-sized particles; nanoparticles act like a complete unit in relation to properties. All materials have some critical range or value below which their properties changes drastically. Particles below 100 nm in diameter show properties that are different from those of conventional solids. When all the dimensions of the particle are in nanometer range, it is known as is dimensional nanoparticles, for example spherical nanoparticles of silica. The definition of nanoparticles may differ for different fields and different materials. From theoretical point of view, nanoparticles are frequently called Nano clusters or simply clusters which are defined as the combination of millions of atoms or molecules. These atoms or molecules may be of same or of different kind. Nanoparticles can be of amorphous or crystalline form and their surfaces can act as a carrier for liquid droplets or gases. The drugs can dissolve, entrap, encapsulate or attach to a nanoparticle matrix. NPs have properties in between those of the bulk material and the atomic or molecular structures.

Nanoparticles should be considered as a distinct state of matter such as crystalline nanoparticle forms (fullerenes and carbon nanotubes) and traditional crystalline solid forms (graphite and diamond).

A evaluation on nano-particle exposed that the ratio of surface area of nano-particle to the volume of the nano-particle is inversely proportional to the radius of the nano-particle. Therefore, when decrease of the radius of the nano-particle, this ratio will increase leading to an increased rate of reaction and the concentration of the pollutants is decreased. The catalyst increases the rate of reaction by adsorption of reactants in such a form that the activation energy for reaction is reduced far below its value in unanalyzed reaction. Copper was considered for this research work as it is cheaper than platinum, palladium and rhodium. Catalytic converters with a spray of copper nano-particle on copper sieve lead to much higher performance of automobiles and reduced pollution in atmosphere [3]. Catalysis involves the process of modification of a chemical reaction rate, most of the times, accelerating the reaction rate by a substance known as a catalyst which is not consumed throughout the reaction. Generally, the catalyst works in the reaction by interact with one or more of the reactants and at the end of process; it is normally regenerated without any changes.

B. Bimetallic Nanoparticles

Bimetallic nanoparticles; composed of two different metal shave drawn a greater interest than the monometallic nanoparticles from both scientific as well as technological point of view [4][5]. Constituting metals and their nanometric size determine the properties of the bimetallic nanoparticles. These are synthesized by the combination of different architectures of metallic nanoparticles. They actually offer us the tendency of optimizing the energy of Plasmon absorption band of metallic mixture which offers us a multipurpose tool for biosensing. These properties may differ from those of pure elemental particles and include unique size dependent optical, electronic, thermal and catalytic effects. Extensive studies in the field of bimetallic nanoparticles started just a decade back. Different methods have been proposed for their preparation and detailed characterization.

These days' researchers are focusing on selectively preparing new bimetallic nanoparticles in different forms, such as alloys, core-shell and contact aggregate. Actually, through bimetalization, the catalytic properties of the resulting nanoparticles can be improved to great extent which may not be achievable by the use of monometallic catalysts. In bimetallic catalysts, the electronic effect plays an important role which describes the charge transfer. Alloying of the constituting elements can result in the structural changes of the bimetallic nanoparticles. From monometallic to bimetallic nanoparticles, an extra degree of freedom is introduced [7]. The catalytic activities of different bimetallic nanoparticles have been subsequently compared. Different methods and correlations have been developed with the help of physical and spectroscopic measurements. The preparation conditions determine the structure and miscibility of the two metals in bimetallic nanoparticle. Generally, bimetallic nanoparticles are

prepared by simultaneous reduction of two metal ions in the presence of suitable stabilization strategy such as steric hindrance and static-electronic repulsive force. In this method, a particle structure between core shell and homogeneous alloy depending on the reduction condition is obtained. By controlling the size, shape and structure of the nanoparticles, we can have control over the reduction rates of the two components.

C. Methods of Synthesis of Nanoparticles

Researchers have discovered many new methods to prepare nanoparticles which are of the required size, composition and shape because these factors greatly influence the properties of the material. Some of the methods used for the synthesis of the nanoparticles are:-

- I. Thermal and photochemical decomposition
- II. Electrochemical reduction
- III. Chemical reduction
- IV. Sputtering
- V. Sol-gel method
- VI. Chemical precipitation method
- VII. Micro-emulsion method
- VIII. Hydrothermal method

III. VARIOUS BIMETALLIC NANOPARTICLES

Researchers are synthesizing novel bimetallic nanoparticles to get desired properties. Various types of bimetallic nanoparticles are:-

A. Platinum based bimetallic nanoparticles

Platinum nanoparticles are now being used in the upcoming generation for automotive catalytic converters due to high surface area, thus the amount of platinum required for their fabrication is less. To enhance the effectiveness of Pt-based electrodes, the Pt based bimetallic nanoparticle catalysts have been synthesized [8][9]. The Pt-X (X = Cu, Au, or Ag, etc.) alloys are very important due to their high catalytic efficiency. In the recent years, polymer-protected colloidal Pt-Cu particles have been prepared and these can be used for the catalytic hydrogenation of solution, where the bimetallic clusters are used as active and selective agents for the hydration of acrylonitrile to acrylamide as well as for hydrogenation of 1,3- cyclooctadiene to cyclooctene [5]. It has also been found that Pt-Cu bimetallic catalysts are effective in the reduction of NO_x. Studies about Pt-Cu based bimetallic nanoparticles have revealed their heterogeneous catalytic activities for reduction of gas phase NO with hydrogen as the reducing agent [10][11]. In Pt-based catalyst studies, the addition of other metals to Pt catalyst decreases the amount of need of noble metal, Pt. It also helps in improving its catalytic ability [12].

B. Nickel based Bimetallic Nanoparticles

Metal nanoparticles such as nickel nanoparticles have been intensively used for its catalytic and the magnetic properties. However, Nickel on combination with other metals shows fascinating properties [8]. Catalysts containing nickel are commonly used due to their low cost, high stability and fast

turnover rate. In the past few years, Ni-Sn based bimetallic nanoparticles have been prepared with controlled size and composition. By varying the stoichiometric ratios of Ni and Sn, bimetallic nanoparticles with different composition such as Ni₁₀₀, Ni₇₄-Sn₄₁, Ni₇₅-Sn₂₅, Ni₄₀-Sn₄₀ and Ni₅₀-Sn₅₀ have been synthesized. The Cu-Ni based bimetallic catalyst has been used as an effective method for improving the efficiency of various reactions. Cu-Ni/Al₂O₃ catalysts and Ni-Cu/samarium-doped ceria catalysts have been used which are used for the hydrogenation of carbon dioxide and for steam reforming of methane.

C. Iron based Bimetallic Nanoparticles

From the recent studies, it has been found that the Fe-Cu bimetallic catalyst system has attracted tremendous attention [13][14][15]. It has been reported that this catalyst when supported on MCM-41 showed higher catalytic activity as compared to Cu or Fe when singly supported on MCM-41 [13]. It shows high catalytic activity even after 10 consecutive runs. Other class of iron based bimetallic nanoparticles includes Pd/Fe nanoparticles which have been prepared by chemical precipitation method in liquid phase. With diameters in the range of 30–50 nm, these nanoparticles exhibit excellent catalytic activity for dechlorination of chlorinated methanes such as dichloromethane (DCM), chloroform (CF) and carbon tetrachloride (CT) [16]. For the treatment of chlorinated organic pollutants, nanoscale bimetallic particles (Pd/Fe, Pd/Zn, Pt/Fe, Ni/Fe) have been synthesized in the laboratory.

D. Gold based Bimetallic Nanoparticles

Gold nanoparticles act as an efficient catalyst and biosensors. It is believed that gold containing nanoparticles can be used for increasing the catalytic activity and selectivity. Au/Pd based bimetallic nanoparticles have been recently prepared and they show interesting catalytic, electrochemical and structural properties [17]. In addition to this, bimetallic nanoparticles of gold/copper have also been prepared. These have many applications but are mainly used in medical sensors and biomedicine. Au/Ni based bimetallic nanoparticles in different shapes and forms are prepared and systematically investigated. Extensive studies have been done for synthesizing Au/Ag BNPs. These bimetallic nanoparticles have extensive applications such that they are used in the detection of glucose and it also exhibits property of chemiluminescence [18].

E. Carbon Supported Bimetallic Nanocomposites

Bimetallic nanocomposites supported on carbon are of great interest. Carbon supported bimetallic nanoparticles have reduced surface area which enhances their properties to a large extent. Water contamination is one of the major problems faced by human beings now-a-days. The presence of unwanted material, ions, micro-organisms such as fungi, bacteria and virus, etc. contaminates the water. The presence of perchlorate ion makes the water unsafe for drinking. Nanotechnology provides an alternate to the water purification. When ruthenium-palladium bimetallic nanoparticles are supported on the carbon matrix, they efficiently reduce the perchlorate into

chloride ions under acidic conditions and thus, helps in treating waste or contaminated water containing perchlorate as the major impurity [19]. Au/Pt/C nanocomposites have improved catalytic properties. These are formed by the normal synthetic route. The reinforcing material (Pt + Au) is uniformly distributed on the matrix (Carbon). It acts as a catalyst in the electro-oxidation of glucose and helps in increasing the rate of reaction. However, Co/Pt nanoparticles supported on carbon is used for the fuel-cell applications. Ag/Ni-C nanocomposites show higher oxygen reduction reaction capacity as compared to the simple Ag/Ni bimetallic nanoparticles. Direct methanol fuel cells are in use from many years but it suffers from certain drawbacks such as high level of poisoning due to platinum anode electrocatalyst. In order to overcome it, new nanocomposites Pt/Au supported on platelet carbon nanofibers (pCNF) has been synthesized and these acts as an effective electrodes for DMFCs, thus, reduces its toxic effects and increases the life span of fuel cell [20].

F. Graphene Supported Bimetallic Nanocomposites

In addition to their activity as a carbocatalyst, graphene based materials are widely used as supports for catalytically active transition metals. Plethora of reactions is being catalyzed using different metal nanoparticles [21]. However, some obstacles are still remaining such as irreversible aggregation during electrocatalytic cycles, leading to a significant loss of nanoscale catalytic effect. Hence, proper catalyst support needed to preserve the intrinsic surface properties. Owing to their extremely high specific surface area which improves the dispersion of the catalytic metals, improved chemical and electrochemical stability at operation temperatures, enhanced electronic conductivity, graphene based materials are appealing choice as catalyst support. Hence, graphene offers a perfect platform for catalytic molecular engineering. In one such example, Kim and co-workers [22] demonstrated that gold nanoparticles (Au NPs) dispersed on graphite oxide were able to catalyze methanol oxidation. It is demonstrated that the GO nanosheets not only serve as structural components of the multilayer thin film, but also potentially improve the utilization and dispersion of Au NPs by taking advantages of the high catalytic surface area and the electronic conduction of graphene Nano sheets. Similarly, graphene has been used as a support for various metal oxides (ZnO, TiO₂, MnO₂, Fe₂O₃, Co₂O₄, etc.) [23] and nanoparticles (Pt, Pd, Ag, Au or alloys) to fabricate hierarchical catalyst systems.

The use of BNPs makes it possible not only to obtain better catalytic activity but also helps in making new materials having desired properties which cannot be achieved by single metal atom. Bimetallic nanoparticles unveil interesting electronic, chemical, biological, mechanical and thermal properties due to the composition and synergistic effects. The activity as well as the selectivity of catalyst is affected by size of the particle. The use of bimetallic nanoparticles may give rise to synergism, when the particles are used for catalysis. The combination of two different metals enhances their specific properties. These properties may be different to those of pure elemental particles. The elemental arrangement of

bimetallic nanoparticles depends strongly on the method used for their production and the system of two metals is generally not in thermodynamic equilibrium. Core-shell bimetallic particles are among the most studied nano-catalysts. Metallic and bimetallic nanoparticles, especially those containing a few tens or few hundreds of atoms, are excellent catalysts because of their highly active surfaces. These catalytic nanoparticles have improved selectivity, efficiency and recyclability, achieving the modern requirement for green catalysts. In the preparation of bimetallic nanoparticles, the interaction between two metals plays an important role [24]. The bimetallic nanoparticles such as Pt-Ag, Pt-Rh, Ag-Ni, Au-Pt, Pd-Au and Ni-Au, etc. has been already prepared.

The extraordinary and unique physical, chemical, and mechanical properties of graphene have led to the development of graphene-based materials for a wide range of applications in different fields. Amongst, the use of graphene-based materials in the field of catalysis has attracted the interests of researchers in the last few years. Due to its extremely high surface area and adsorption capacities, graphene is expected to function as an excellent catalyst support material. Moreover, an ability to tune its structure using desired functionalities have added significant versatility for such materials in metal free catalyst systems. The interest is due to the activity and stability of graphene based catalysts through tailoring its structures/morphologies, catalytic performance, and design for synthesis, catalytic mechanisms. This editorial note summarizes the versatile applications of graphene-based catalysts in organic synthesis as a carbocatalyst, metal free catalysis, in photocatalysis, and as a catalyst support and provides an outlook on future trends and perspectives for graphene applications in sustainable catalysis.

IV. CATALYTIC CONVERTERS WITH NANO-PARTICULAR COATING

To control the emissions from exhaust of having copper nano-particles coated on copper sieve as catalytic converter was used. The engine was designed to run at medium load for a longer time due to less emission of HC and CO. At full load, emission of CO and HC was higher so it is not advantageous to run engine at full load. The converter used two different types of catalyst, reduction and oxidation catalyst. Multigas Analyzer (NPM-MGA-2) was used for the measurement and comparison for CO and unburned hydrocarbon in the exhaust of the engine at various speeds and loads. The idea behind the work was to create a structure that exposes the maximum surface area of catalyst to exhaust stream, also minimizing the amount of catalyst required. [26]. the efficiency of translation was evaluated for a catalytic converter used with spark ignition engine under steady operating situation. Apart from this, three way converters have been compared to understand the influence of substrate particles on the exhaust gas conversions for different operating conditions of vehicle. This research work was based on the evaluation of spark ignition gas emissions upstream and downstream of the catalytic converter [27]. In this research work, many tests were performed on a four stroke engine to compare its performance

in two cases; with and without the use of copper nano-particle coating.

The outcomes uncovered that the copper nano-particle coated engine exhibited a much better performance than a normal engine. During the tests, the catalytic efficiency was found to increase as the size of the nano-particle powder decreased [28]. For pollution avoidance from automobiles and to achieve a clean and green environment, a nano coated catalytic converter was designed and manufactured [29]. Nano particles were effectively employed to reduce surface roughness of engine components and to act as protective coating against wear of components. Apart from this, the importance of nano-coatings for engine applications was analyzed [30]. In this work, different experiments were conducted to improve the performance of the engine and reduce the level of emissions of hydrocarbons and carbon monoxide from automobiles. The focus of the experiments was on evaluating the engine performance parameters and studying the emissions reduction methods for spark ignition engines [31]. Thakur and Saikedkar made some alterations and modifications in the design of a spark ignition engine so as to increase the retention period of exhaust gases to provide more time for its oxidation and in this manner to decrease hurtful outflows. Their approach was to control the exhaust emissions from four stroke, single cylinder and spark emission petrol engine having copper nano-particles [32]

In addition to their activity as a carbocatalyst, graphene based materials are widely used as supports for catalytically active transition metals. Plethora of reactions is being catalyzed using different metal nanoparticles

Recent years' research and development have expanded the applications of carbon far beyond those of the traditional allotropes graphite and diamond, mainly by the discoveries of carbon nanomaterials (CNMs). The most commonly mentioned ones are fullerenes, carbon nanotubes and graphene, but there are also others that are being researched, such as graphyne, graphdiyne, graphone, graphane [33] and carbon quantum dots.

The main application of platinum is in catalytic converters that reduce air pollution from vehicles with internal combustion engines. Several studies discuss the use of graphene and CNT as catalysts. For example, there are reports of graphene being able to replace platinum as catalyst in fuel cells if doped with non-metal atoms such as nitrogen or boron, or used together with relatively abundant metals such as iron and manganese [34]. Apparently, graphene enhances the catalytic activity of such metals. Fuel cells could become an important future application of platinum. Similar reports of catalytic properties, either by being doped or by enhancing the properties of more abundant metals, exist for CNTs [35]. It thus seems that CNMs, either doped by non-metal elements or by working together with non-noble metals, can have similar properties as platinum in catalytic converters. Two theoretical studies have used quantum mechanical modeling to calculate that graphene could function as a catalyst for exhaust gases specifically. One regarded the reduction of nitrogen oxides by nitrogen-doped grapheme [36], and the other regarded carbon monoxide oxidation by graphene oxide.

V. TEST PREPARATION

Before conducting the research and collecting the data, the researcher prepares the following tools to be used in the research consisting of -

- A. Testing Machine- The researcher uses a vehicle machine as the testing machine.
- B. Gas Analyzer- The instrument used to test the exhaust emissions of Carbon Monoxide in this study is Gas Analyzer
- C. Thacometer- This tool is used to find out and see the changes of vehicle engine revs when the researchers do the variation of engine rev on the tested vehicle.
- D. Data Collection Stage- Before collecting the test data, the first thing that needs to do is preparing the standard conditions of the machine with Tune Up, so that the machine is ready to work. At the stage of data collection, the researcher warms the engine to prepare the machine to be ready at the test conditions. The first stage is the measurement without Catalytic Converter. This measurement is aimed to determine the concentration of exhaust emissions of the tested machine released without any additional tools. The measurement is performed three times and each data obtained is recorded, and its results is analyzed next

The steps are as follows: firstly, the machine is turned on, idle rotation, measuring plug is inserted into the mouth of the exhaust, and then step on the gas pedal and read the motor rpm display, after that read the display on the gas analyzer test tools take note the measurement numeral results on the display, repeat the step two for different rpm variations; 1000, 1500, 2000, 2500, 3000, back to 2500, 2000, 1500, 1000 and until the idle rotation returns and at each different rpm measurement the gauge plug is pulled from the exhaust vent. Once the measurement without Catalytic Converter is completed, it is followed with the measurement of Catalytic, with the same steps.

As long as there is an extensive use of scarce chemical elements a “dining at the periodic table” there will always be problems related to critical and scarce materials. Considering bimetallic nanoparticles and bimetallic nanocomposites which are formed by carbon or graphene as a catalyst in catalytic converter in place of scarcer materials could be beneficial from a resource use perspective.

VI. CONCLUSIONS

Catalytic converter design and modification of catalytic materials can be an alternative to overcome the high air pollution problem from the automotive and chemical reactor sector, especially particular Carbon Monoxide and hydrocarbon exhaust emissions. The use of bimetallic nanocomposites as a catalyst in the catalytic converter was significantly able to increase the reduction of Carbon Monoxide and hydrocarbon from exhaust emissions.

Researchers are trying to synthesize more and more new bimetallic nanoparticles with desired and controlled geometrical as well as magnetic properties. It can also be concluded that bimetallic nanoparticles are of greater

importance as compared to other because of enhanced properties. These particles have greater surface area, as a result of which they act as catalyst and helps in effectively catalyzing various reactions.

In order to increase the effectiveness and properties of bimetallic nanoparticles, these are converted into nanocomposites which are formed by supporting them on the organic (carbon or graphene) counterparts. Brief discussion about bimetallic nanocomposites exhibits that these are more important than bimetallic and monometallic nanoparticles.

The thought behind the work is to make a structure that exposes the larger surface area of catalyst to exhaust flow and also reducing the amount of catalyst which is required in process. One is using the nano-catalysts with increased surface area for gaseous reactions. Catalysts work by speeding up chemical reactions that transform harmful gases from automobile and industrial plants into harmless gases. To accomplish this goal, in catalytic converter using bimetallic nanoparticles and bimetallic nanocomposites as a catalyst. The catalyst increases the rate of reaction by adsorption of reactants in such a form that the activation energy for reaction is reduced far below its value in non-catalytic reaction.

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