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Review Paper

Nanoparticle-Membrane Filtration of Vehicular Exhaust to Reduce Air Pollution – A Review

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Abstract

Vehicles that run on fossil fuels emit an enormous amount of greenhouse gases. The oxides of carbon and nitrogen are main contributors of air pollution which are due to incomplete combustion, from the engine. Oxides of carbon and nitrogen are emitted in significant quantities from vehicles, which pollute the environment. In this review, design of nanoparticle embedded nano-membrane-filter has been proposed to reduce air pollution from the vehicular exhaust. The membrane would be placed in the exhaust system of the vehicle, which traps the harmful gases thereby reduces air pollution. The life-time of nanomembrane is known to be very high.

Keywords: Nano-particle, nano-membrane-filter, air pollution, carbon, nitrogen.

Introduction

Vehicular exhaust has been a major source for air pollution for a long time. Across the world, the personal vehicle is actually the greatest pollution contributor. It is the same effect of this one vehicle which when scaled up across the entire world gets multiplied many folds resulting in a million vehicles causing a pollution disaster[1]. The negative effect of automotive emissions does not affect only the person driving but also the others around them. Various greenhouse gases such as carbon dioxide, methane, nitrous oxide and other gases like chlorofluorocarbon (CFCs) are emitted. The gases act like a blanket and increase the global temperature which is otherwise called as global warming. The planet's thermostat had been set at a pleasant average temperature of 59°F for the last 10 years and recently it is increasing rapidly[2]. A typical engine combustion process is represented below[3].

$$\text{Fuel} + \text{Air} \rightarrow \text{Hydrocarbons} + NO_2 + CO_2 + CO + H_2O \quad (1)$$

Hydrocarbon emissions are the fragments of fuel molecules, which are only partially burnt.

Various exhaust gases and their effects

Nitrogen Oxides: Converters basically are used to break down gases. A higher percentage of nitrogen-dioxide (NO_2) is formed as product compared to carbon-dioxide. NO_2 makes up about 7.2% of the gases that cause global warming[3]. But these converters, though break down molecules, they emit a higher quantity of their oxides into the atmosphere.

Carbon Monoxide: Most CO gas is produced when the fuel is not combusted properly in the engine. This happens when there is an insufficient flow of air into the engine[4]. This occurs when the vehicle is under prolonged use, in mountains where the oxygen content is comparatively low or by general ageing of the engine itself. Two-third of carbon monoxide emissions come from transportation sources, mainly from the urban areas where the population is high.

Carbon Dioxide: Originally carbon dioxide viewed as a product of perfect combustion, but now, it has become a pollution concern. Carbon dioxide is a greenhouse gas that traps the earth's heat and contributes to global warming.

Nanomembrane Fabrication

Nano-material fabrication is a very intricate process. It involves various steps like selecting the cost effective material for fabrication, suiting to required conditions like heat resistant. The pores of the nano-membrane are also very important and care has to be taken to design the pores according to the requirment[5]. When it comes to fabrication of the membrane for a silencer, the material that could be heat resistant, which does not disintegrate the prolonged exposure to hot gases has to be considered. The membrane should also have the appropriate pore distribution for an optimum absorption process.

Pore Size Designing

The nanomaterial can be effectively used for various applications if its pore size is controlled. Some applications require smaller pore size while other applications require larger pore size. The pore size can be controlled by treating the nano-membrane with various surfactants during or post fabrication process. Asymmetric and symmetric pores can be formed by various processes. During the fabrication process itself, the membranes must be treated in a specific manner either by a solution or by any other physical means which can form the pores on the nano-membrane's surface. Some use acidic reagents which react with membrane and oxidize surface layer, hence resulting in the formation of smaller pores. The membrane can also be pre-treated with any photosensitive material such as photo-silica when exposed under a stream of strong UV rays will result in opening up of more pores on the membrane's surface[6]. Time taken and pore size produced against different concentrations of the etching solution are shown in tables. By varying the etchant component concentrations, it is possible to control the degree of openings[7].

Table-1
Time for etching versus Concentration of etchant[8]

Etching Time	Concentration of NaOH in surfactant-doped etchant	
	4 M	6 M
T1	4 min 12 s	2 min 29 s
T2	6 min 0 s	3 min 30 s
T3	7 min 43 s	5 min 0 s
T4	9 min 30 s	6 min 32 s

Table-2
Pore size versus Concentrations of etchant[8]

Etching Time	Concentration of NaOH in surfactant-doped etchant	
	4 M	6 M
T1	60	66
T2	92	109
T3	101	172
T4	137	207

COx and NOx Absorption

Nationwide, 77% of CO emissions are from transportation sources. The largest emissions contribution comes from highway motor vehicles. Nitrogen dioxide a brownish, highly reactive gas present in all urban atmospheres. The oxidation of nitric oxide (NO) in the higher layers of atmosphere due to the heat from the sun and earth, leads to the formation of nitrogen-dioxide[8]. Nitrogen oxides (NOx) include various nitrogen compounds like nitrogen dioxide (NO_2) and nitric oxide (NO). These compounds also play an important role in the formation of acid rains. Individually, they may affect ecosystems, both on land and in water[9]. NOx is formed when fuels are burned at high temperatures. From the literature studies, it is proved that the molecular size of carbon dioxide and nitrogen dioxide are different. By using this molecular size difference, the oxides of carbon and nitrogen can be removed as separate layers by suitable molecular sieve.

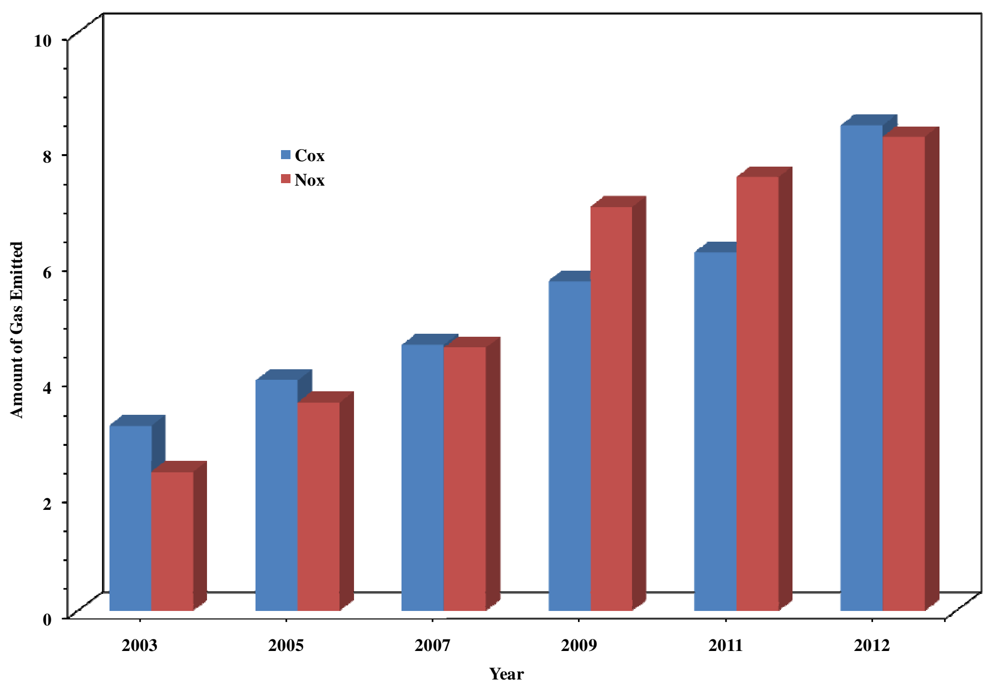

Figure-1
A statistical data showing the amount of oxides of nitrogen and carbon monoxide emitted from vehicles in a span of 10 years[2]

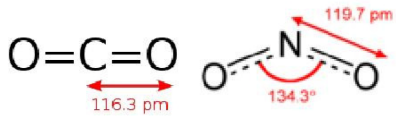

Figure-2
The bond length of CO_2 and NO_2 are shown for comparison[3]

For separation process, the material that absorb carbon-dioxide has to be given prime consideration. Carbon-dioxide is reactive to minerals like zinc, calcium and magnesium. The absorption and release of carbon-dioxide is a temperature controlled process[10]. Since it is in a gaseous form, it reacts faster in an alkaline-based media. Thus the hydroxides of calcium and sodium can be used to absorb carbon-dioxide. The trapped carbon-dioxide can be later released in a controlled environment by treating the membrane at a higher temperature[11]. Separation of gases by nano-membranes, seems to be more promising, mainly due to lower energy requirements and intensive development in various countries.

Porous materials like zeolites are known for its different shapes and pore sizes that determine which molecules get absorbed into the material. Like molecular sponges, porous materials can also be reused in a cycle of capture and release[12]. For instance, in the case of carbon capture, once the material is saturated and cannot absorb any more CO_2, the gas can be extracted. It has been found that though siliceous zeolites are composed of the same tetrahedral blocks of silicon and oxygen atoms, their geometrical arrangement differ from one to the other.

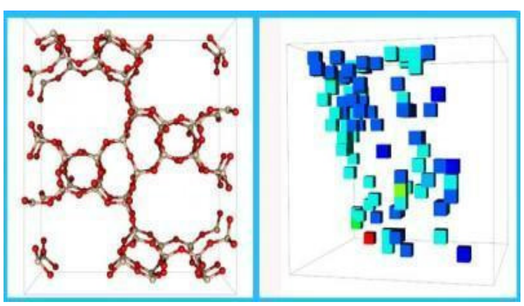

Figure-3
Left: This image shows of silicon (tan) and oxygen (red) atoms. Right: The cavities of the structure shown on the left. The colored points show how many times a certain shape appears in the structure[14]

A porous structure can be characterized based on the size of its largest pore or its total volume of empty space. Using this technique the pathways between atoms and its path network can be analyzed.

Suggested Nano-Absorptive Materials

The nanomembranes act as molecular sieve to absorb gases. It is made with materials like an aluminosilicate compound known as zeolite and used to divide the substances on a molecular stage. Similarly, like sieve that can be used on segregating the sand from rocks, a nano-molecular sieve separates larger molecules from those smaller ones. When two molecules have similar size, the molecular filter could also set aside the molecules depending on their polarity. Compared to filter that is used in separating the sand from rocks; the nanosieve restricts the smaller molecules on passing over them. Instead, these molecules will be absorbed directly by the filter. The empty distances within the shift structure and pores hold and trap the smaller molecules. Thus, the efficiency of a sieve will not depend on how the pores look on the available space within the structure of the sieve. A nano-molecular sieve could absorb around 24% of their mass. The structure looks crystalline in appearance and the absorbent material with in a molecular sieve has totally uniform pore sizes[13]. On the other hand, the sizes of the pores will depend on the kind of shift. There are different types that include an insulated glass molecular sieve, types 3A to 5A as well as type 13X. 3A and 4A are known as the general drying agents. 3A is commonly used in drying and dehydrating the hydrocarbons. 4A sieve is used in the closed systems such as electrical components as well as drug packaging to gain sure dryness. 5A sieve is used in removing the unnecessary hydrogen sulfide, an extremely hazardous gas and carbon dioxide coming from the natural gases[14]. Because carbon dioxide is a very important factor contributing to global warming, carbon dioxide storage and conversion have attained great importance in the scientific community and the public[15]. One of the main strategies for CO_2 management is the direct capture of CO_2 from the source of emission. The other strategy is its adsorption on reactive substrates like zeolites and metal oxides and conversion to industrially useful products such as carbonates, bicarbonates, ethanol, and formic acid.

Zeolite: Zeolites are crystalline, porous aluminosilicates that are extensively used in catalysis, chemical separations and as adsorbents. When the size of the zeolites is less than 100 nm, then they fall under the nanocrystalline zeolite category. Due to their small size, nanocrystalline zeolites have unique properties such as high surface areas, high concentration of reactive sites on the external surface and enhanced diffusional properties. Zeolites can be ideal for the large scale sequestering and conversion of CO_2 to more useful products[16]. Recent studies indicated that these nanocrystalline zeolites can be used for wider applications more towards environmental pollutions. Faujasite zeolites (e.g. NaY) are considered promising environmental catalysts because of their ion exchange capacity and pH properties. NaY zeolites have shown enhanced performance for the selective reduction of NOx. (NOx = NO + NO_2) with urea.

Metal Oxides: Mineral dust aerosol in the atmosphere consists of different types of metal oxides. Metal oxides are of great importance as an environmental interface. They act as heterogeneous catalysts where surface reactions of carbon dioxide can be carried out.

Zinc: Zinc is another important naturally occurring mineral which exists in the form of important minerals such as sulfides, carbonates and oxides. The applications of zinc oxide powder in industry are numerous. Recent studies of CO_2 adsorption on ZnO surface have shown the formation of an unusual tridentate carbonate species with the two oxygen atoms of the CO_2 molecule being almost equivalently bound to two different Zn surface atoms[17]. Mathematical equations and calculations provide insights into the molecular structure of the carbonate, bicarbonate and carboxylate product formation as a result of reaction of CO_2 with the metal oxide surfaces.

Magnesium: Another metal oxide, which is equally important in the Earth's crust, is MgO. It is also used for numerous applications in catalysis, refractory material industries, paint, and superconductors. Recently, MgO is also considered as a promising sorbent for chemisorption of various pollutants. Moreover alkaline earth-based oxide materials[18] have received increased attention as adsorbents for CO_2[19]. In the case of MgO, stoichiometric amounts of CO_2 can be taken up according to the reaction.

$$MgO + CO_2 \rightarrow MgCO_3 \quad (2)$$

Efficiency

From the literatures on CO_2 capture by adsorption, it can be understood that to develop an appropriate CO_2 capture adsorbent should satisfy i. low-cost raw materials, ii. low heat capacity[20], iii. fast kinetics, iv. high CO_2 adsorption capacity, v. high CO_2 selectivity and vi. thermal, chemical, and mechanical stabilities[20] .The adsorption efficiencies of zeolites are largely affected by their size, charge density, and chemical composition of cations in their porous structures. Accordingly, a number of reports focus on zeolites with highly crystalline structure, high surface area, and 3-dimensional pore structures by altering their composition as Si/Al ratio. Another research field focuses on the exchange with alkali and alkaline-earth cations in the structure of zeolites to enhance the CO_2 adsorption. In recent literatures, the improvement of CO_2 adsorption capacity and cyclic performance of the calcium based adsorbents are proposed by i. reactivation by steam hydration, ii. incorporation of inert materials, and iii. modification of pore structure[20]. The reactivation of CaO by steam hydration process could lead to an increased pore volume and an improvement of cyclic performance.

Conclusion

Owing to huge amount of the CO_2, chemical absorption may be more suitable than physical absorption purpose. However, chemical absorption is an energy intensive process in which more than 60% of total energy consumed in stripper for thermal regeneration of CO_2-rich chemical absorbents. Various methods like chemical looping combustion (CLC) and rotating packed bed method use many sophisticated apparatus to absorb carbon-di-oxide. Other methods include the use of cryogenics or solvents which require very strict conditions perform an efficient absorption. To make absorption as practical application, the future research could be focused on the improvements of absorbent formulation and process efficiency. To achieve the purpose, the following approaches are suggested: i. to use absorbents with less corrosion, less viscosity. low vapor pressure, rapid reaction rate with CO_2, high CO_2 absorption capacity, and less regeneration energy, a compromised formulation is needed because all the mentioned properties may not be satisfied in the meantime, ii. to enhance high gas-to-liquid mass and heat transfer rates in absorber and stripper, iii. to reduce equipment volume and capital cost, iv. to prevent the negative effects of SOx, NOx, and oxygen on absorbent[16], and v. to develop a more suitable model for the scale up purpose. The nanoparticles discussed in this paper have capabilities to absorb carbon dioxide and nitrogen dioxides. These when embedded onto a nanomembrane filter, acts as an absorbent to these greenhouse gases. By proper distribution of the particles and suitable placement of the nano-membranes in the vehicle could have been the efficient absorption process.

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