



An overview on metal-oxide catalytic converters

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Article history

Received 15.08.2020

Accepted 15.10.2020

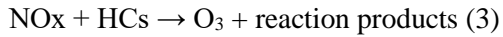
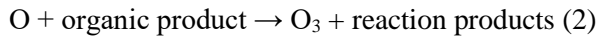
DOI <https://doi.org/10.26825/bup.ar.2020.002>

Abstract: Diesel vehicles produce exhaust gases that include nitrogen oxides (NO_x), carbon monoxide and hydrocarbons. A major environmental problem is the elimination of nitrogen oxides, as they are major air pollutants. Global restrictions on NO_x emissions from fuel combustion have been imposed. Efforts have been made to develop catalysts for the selective catalytic reduction of NO_x. In this paper is presented the types of catalytic converters used nowadays for dissipate emissions and selective catalytic reduction.

Keywords: catalytic converter, exhaust gas, two-way converter, three-way converter, selective catalytic reduction, catalysts

1. Introduction

Eugene Houdry, the french engineer, was the first one invented the catalytic converter. Later, catalytic converters were improved by other engineers, such as Carl Keith, John Mooney, Rodney Bagley and Irwin Lachman, making the first production of catalytic converters in 1973 [1-3]. The catalytic converter was introduced in 1975 on a large scale in automobiles to comply with the regulations on exhaust emissions. Catalytic converters are used to reduce pollutants. The main pollutants in the exhaust gases are carbon monoxide, hydrocarbons and nitrogen oxides.. Hydrocarbons and carbon monoxide occur due to incomplete gas mixing, as the combustion efficiency is <100%. Nitrogen oxides are formed during very high temperatures (>1500°C) of the combustion process, causing the thermal fixation of nitrogen in the air. The chemical storage phase takes place during normal engine operation [4]. The exhaust gas temperature during the storage of nitrogen oxides varies from 150°C to 450°C, depending on the engine operating point (speed and load). Nitrogen oxide is oxidized to form nitrogen dioxide (NO₂) [5]. Once the catalyst has reached the maximum storage capacity of nitrogen oxides (NO_x), it proceeds to the regeneration phase. In this case, the engine runs on a rich mixture, the exhaust temperature being between 200°C-500°C. The rich mixture is necessary for the presence of hydrocarbons (HC) and carbon monoxide (CO) in the catalyst, elements that contribute to the chemical reactions of reduction of nitrogen dioxide (NO₂) [6]. Photochemical reactions are triggered by the decomposition of NO₂ into NO and atomic oxygen under the influence of light that reacts with hydrocarbons, which form ozone and various oxidation products presented in the reactions below:



Exhaust emissions from the engine must be strictly controlled due to the consequences for the environment and health. The most effective way to control exhaust emissions are catalytic converters with different types of catalysts that convert the exhaust into water, carbon dioxide and nitrogen. Over time the catalysts have gone through several stages of development.

2. Types of catalytic converters for car exhaust emissions

The development of catalysis was initially associated with catalytic oxidation, and later as part of several chemical processes [7]. Due to the differences between gasoline and diesel in terms of exhaust environment, the oxidizing catalytic converter has developed in two directions as follows: gasoline applications have evolved from two-way converters to three-way converters; at the same time, oxidizing converters have progressed to diesel oxidation converters with other downstream pollution control devices responsible for reducing regulated emissions for diesel counterparts. "Oxidizing" or "bidirectional" converters were the oldest converters that existed since the 1970s, as oxidations of hydrocarbons and carbon monoxide took place over the catalyst. Oxide emissions could not be controlled using these older converters. Because researchers had to focus on HC and CO, standards for nitrogen oxide emissions were left out of the regulations. They came back in 1981, when the same catalytic system had to convert NO_x to N₂ [8]. This is how "oxidizing" or "bidirectional" converters have been replaced by three-way catalytic converters. For petrol vehicles, oxidizing converters were used for the first time to limit exhaust emissions. At that time, diesel cars were not required to have that technology because they already had low emissions of hydrocarbons and carbon monoxide [9]. On the other hand, the use of the oxidation catalyst has been extended to diesel cars as diesel oxidation catalysts [10]. Over diesel oxidation catalysts, HC and CO oxidation is clear, except that it has the role of converting NO to NO₂, which participates in the regeneration of the particulate filter and improves the downstream NO_x reduction process.

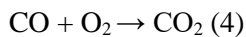
2.1. The three-way catalyst

When NO_x emission standards came into force, the same catalytic system that supplemented oxygen to hydrocarbons and CO had to remove oxygen from NO_x to result in nitrogen (N₂). The first NO_x reduction to N₂ was performed on a platinum / rhodium catalyst [11]. A pump connected to the three-way catalyst supplies air between the oxidation and reduction catalysts. But this solution has not been technically and economically accepted. It has been observed that under certain favorable fuel conditions the platinum / rhodium catalyst can simultaneously convert CO and HC and reduce NO_x with great efficiency. This catalyst approach has become known as a three-way catalyst (TWC) [11]. The transformation of the three pollutants into less harmful gases through a single TWC became feasible when the composition of the exhaust gases could be kept close to the stoichiometric point. At present, modern gasoline cars with three-way catalysts can achieve the elimination of exhaust gases [11].

2.2. The two-way catalyst

Patina-based catalysts have emerged as a solution for controlling catalytic emissions, which has led to a major reduction in hydrocarbon and carbon monoxide emissions [11]. Platinum deposited on the aluminum oxide substrate covered on a honeycomb support so that it can be placed on the exhaust manifold in front of the muffler, as close as possible to the engine [12]. These models were essentially bidirectional oxidation catalysts, as they helped both HC and CO react with the remaining oxygen in the exhaust having two simultaneous roles:

- ✓ oxidation of CO in CO₂;
- ✓ oxidation of hydrocarbons to CO₂ and H₂O.



Until 1981, bidirectional catalytic oxidation converters were mainly used on petrol cars, and since then they have been replaced by three-way catalysts as they could not control nitrogen oxides [13].

2.3. Diesel oxidation catalyst (doc)

With the advent of regulations limiting harmful emissions into the atmosphere by diesel engines, the diesel oxidation catalyst (DOC) became part of diesel exhaust systems [14]. Volkswagen, one of the world's largest automakers, voluntarily introduced in 1989 the first DOC application on a new car, the Golf model "Umwelt with diesel engine adding platinum-based diesel oxidation catalysts, in a similar way to conventional two-way petrol catalysts [15]. The emergence of the stricter Euro 3 standard (2000) has made this device mandatory for all diesel cars [16]. The operating requirements for DOC are different from those for TWC, as the exhaust temperature for gasoline engines is usually higher than for diesel counterparts. DOCs operating at low temperatures have to operate in lower temperature conditions have 2 ~ 3 times the amount of catalytic material as a TWC for the same amount exhaust gas cleaning [17].

2.4. Selective Catalytic Reduction (Scr)

Through TWC, NO_x is controlled from the release to the exhaust system in stoichiometric conditions [18]. Even so, it cannot achieve NO_x elimination when gasoline and diesel engines have low combustion [19]. Currently, selective catalytic reduction is the main technical remedy for diesel [18]. The SCR reaction requires a reducing agent to control nitrogen oxides. NH₃ one of the reductants selectively reduces NO_x using specific catalysts [18]. In mobile applications, ammonia-smelling gas has had to be replaced with a precursor, such as urea that can be stored safely [18]. Other reducing agents have been proposed to avoid the handling of ammonia. SCRs can be classified according to the reductants used in three groups as follows: HC-SCR; H₂-SCR; NH₃-SCR [20]. Of the three categories mentioned above, the best choice is NH₃-SCR. The use of urea to reduce the exhaust emissions of diesel engines has been applied since 1988 [21-23]. In 1985 urea was already used as a precursor for stationary SCR applications [24]. In 1990, the first researches on urea-mobile SCR were revealed. Due to the characteristics of urea (it is neither toxic nor corrosive) it is found in aqueous solutions, such as urea-water known as AdBlue®, and is used for diesel applications. [25, 26].

Currently, major car manufacturers have adopted the option of adding urea solution to an additional tank so that it decomposes in the presence of hot gas flow after the solution is previously sprayed into the main exhaust pipe.

3. Types of materials used for catalysts

The three main categories in which the catalysts used in the SCR process can be generally grouped as follows: noble metal-based catalysts; metal oxide catalysts and zeolite-based catalysts.

3.1. Noble metal-based catalysts

Pd, Pt, Au and Rh as noble metal catalysts are used as support TiO_2 , ZrO_2 , SiO_2 and Al_2O_3 , which are used for selective catalytic reduction. Noble metal catalysts have a higher activity and special properties at low temperatures. The disadvantage is that some of the NH_3 will be oxidized by the noble metal catalyst, and the SCR system that uses this type of catalyst will increase the cost of the system. The basic reaction process is NO deoxidation at the active site of the Pt catalyst, and Pt-O is limited by reduction [27]. Zhang et al. synthesized by the impregnation method a series of catalysts supported with TiO_2 with 0.5% by weight of noble metal (Pd, Pt, Ru and Rh) using propylene as a reductant. They studied catalysts by comparing their catalytic performance. The results of the experiment showed that the highest catalytic activity was the Pt / TiO_2 catalyst had. For the Pt / TiO_2 catalyst the elimination rate was 63% at 140°C, achieving 100% of the propylene conversion. At temperatures of 200°C and 225°C respectively, the NO_x removal rates of Pd/ TiO_2 and Ru / TiO_2 catalysts were lower than those at 140°C for the Pt / TiO_2 catalyst. The conversion rate of propylene was in the order of Pt / TiO_2 (160°C)> Pd / TiO_2 (240°C)> Ru / TiO_2 (250°C)> Rh / TiO_2 (300 °)> TiO_2 (350°C). The results of the experiment showed that the specific surface area of the catalyst produced by impregnation synthesis was smaller than that of hollow TiO_2 , and this can be explained by the fact that the noble metal has a less specific surface area. As the temperature increased, the conversion rate from NO to NO_2 increased. In the low temperature range the Pt / TiO_2 catalyst had higher oxidability than other catalysts. [28, 29].

Yang et al. synthesized the Pt / Al_2O_3 catalyst by impregnation synthesis and studied the effect of Pt temperature and load on the reaction. The results showed that only N_2O was formed from low chemisorbed NO molecules at Pt. Compared to N_2O N_2 formation was specific at temperatures above 80 °C [30].

Valanidou et al together with Olympiou et al. synthesized the catalysts Pt / MgO-CeO_2 and Ag / $\text{MgO-CeO}_2\text{-Al}_2\text{O}_3$, respectively. The results showed that the catalysts showed a high NO conversion rate, selectivity and high N_2 stability. After 48 hours of reaction in flow, the active sites of the catalyst were not affected by the presence of SO_2 , which shows a high stability of the Ag / $\text{MgO-CeO}_2\text{-Al}_2\text{O}_3$ catalyst [31, 32].

3.2. Oxide materials for catalysts

The most efficient catalysts for NH_3 -SCR are those based on metal oxides whereas the use of Pt-based catalysts has been quite limited as its optimal temperature range is small [33]. Due to their excellent activity, selectivity and stability of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts have been intensively studied [33]. Their major disadvantages are high activity for unwanted oxidation of SO_2 , high toxicity of vanadium and inefficiency at low and high temperatures [34]. For the SCR process the most used catalyst is V_2O_5 dispersed on the TiO_2 anatase support promoted by WO_3 (and /or MoO_3). In general, the total surface area of the catalysts is 50-100 m^2/g , with a V_2O_5 content of 0.5-3% and a MoO_3 or WO_3 content of 5-10%. Studies conducted in IR and Raman show that vanadium, tungsten and molybdenum species are present on the surfaces of these catalysts [35]. For automotive applications the catalyst should cover a wide range of temperatures, because during the cold start the engine is low and during the exotherm regeneration of the particulate filter is increased..

Iron oxide, as a catalyst, has been intensively studied in recent years due to its characteristics, namely, low toxicity and thermal stability [36].

For example, Shen et al. used the sol-gel method to dope Mn-Ce / TiO₂ with iron to elaborate a Fe-Mn-Ce /TiO₂ catalyst. Fe addition has been shown to improve NH₃-SCR activity at low catalyst temperature [37].

Liu et al. developed α -Fe₂O₃ and γ -Fe₂O₃ powder by coprecipitation synthesis and compared the catalytic activity and selectivity of both phases of ferric oxide under the same conditions. The results showed that at a temperature between 150-300 ° C higher catalytic activity had the catalyst γ -Fe₂O₃. Ammonia and nitrogen oxide were adsorbed and reacted easily with γ -Fe₂O₃. Impairment of the SCR reaction occurred by blocking active sites due to nitrate formation [38]. Wang et al. they synthesized the Fe₂O₃ powder by the aqueous precipitation method. The results showed that due to the presence of SO₂ the deactivation of Fe₂O₃ took place and in 6 hours the NO conversion decreased from 99.2% to 58%, as SO₂ gradually decreased the activity of the catalysts. The results showed that the suppression of catalytic activity can be explained by the inactivation caused by SO₂ which is due to the formation of metal sulfates and ammonium sulfates on the surface of the catalyst during the chemical reaction [39].

3.3. Zeolite-based catalysts

Recently, zeolite-based catalysts are becoming more and more interesting, especially zeolite-based catalysts with metal ion exchange, such as Fe-ZSM-5 and Cu-ZSM-5, because has high activity and durability [40].

Delahay et al. investigated both Fe zeolite and zeolitic systems. The results showed that iron-exchanged zeolites showed activity at high temperatures, and those replaced with copper had a good activity below 300 ° C, because above 350°C, NO conversion decreases due to the oxidation process of ammonia [41,42].

Schay et al. developed a series of Cu-ZSM-5 catalysts and their studies showed that a catalyst with a copper ion exchange of 132% at a temperature of 300°C, the maximum conversion of NO was 70%, and at a temperature between 200°C and 300°C its catalytic activity was better than those with 88% copper ion exchange. As the exchange of copper ions increases, the number of oxidations increases, which leads to the formation of NO₃-type surface complexes of the active intermediate. The catalytic activity of the Cu-ZSM-5 catalyst has been improved [43].

Li et al. investigated metal oxide catalysts, zeolite (Fe/Cu) and the reaction mechanism of NH₃-SCR and showed that the resistance of metal oxide based on H₂O and SO₂ based on Mn is a major problem for its use at low temperatures [44].

In the literature, the authors are reluctant to use zeolite-type catalysts for the direct decomposition of NO because they show low SO₂ resistance.

4. Conclusions

Catalytic converters have been used in vehicle emissions control for many years, e.g., three-way catalytic (TWC) converters in spark-ignition engines during the past several decades and DOCs in diesel engines since the 1990s. Catalytic converters are used to reduce exhaust gases. Exhaust gases contain hydrocarbons, carbon monoxide and nitrogen oxides. The most effective way to control exhaust emissions are catalytic converters with different types of catalysts that convert the exhaust gas into water, carbon dioxide and nitrogen. The catalyst efficiency reduces at high exhaust flow rate and also the catalyst ages over time. Selective catalytic reduction can be classified according to the reductants used in three groups as follows: HC-SCR; H₂-SCR; NH₃-SCR. The catalysts used in the SCR process can be generally classified as follows: noble metal catalysts; metal oxide catalysts and zeolite-based catalysts. The catalyst types could be a base metal (e.g., copper, Cu, or chromium, Cr)

but are more usually noble metal (platinum, Pt, palladium, Pd, rhodium, Rh). The transition metal oxides of copper, cobalt, iron chromate, and vanadium are also useful as catalysts and have been considered.

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