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Automotive Internal Combustion Gas Reduction using CuZSM-5 in a Catalytic Converter

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Toxic gases emitted by internal automotive combustion are responsible for air pollution and deterioration of human health. Therefore, in this study modified zeolite was evaluated as an alternative catalyst for reducing automotive gases in a catalytic converter. For the study, the CuZSM-5 zeolite was synthesized by the hydrothermal method, exchanged with copper ions and then installed in the exhaust of a T3 Bi-Fuel engine. The experiments were carried out on an auto model 1984 Toyota, with and without a catalytic converter at different revolutions per minute (rpm) as idle, average and maximum, using the HGA 400 4GR gas analyser to measure hydrocarbon (HC) and carbon monoxide (CO). The results showed a significant reduction in LPG engine of Hydrocarbon Propane (78 %) and CO (60 %) at high rpm; while in gasoline engine was reduced at Hexane (29 %) and carbon monoxide (68 %) at low rpm. This showed that Cu-zeolite is efficient in reducing gases and more economical than the commercial converter.

1. Introduction

The expansion of cities, the industrial sector and natural factors, each year release millions of tons of air pollutants (Pourvakhshoori, 2020). Of these, the automobile fleet is the main source of emission of toxic gases such as carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO_X) (Bello, 2020). Multiple studies have shown that humanity is exposed to poor air quality on a daily basis (Sánchez, 2012), inducing respiratory and heart diseases (Valverde, 2016) and irreversible changes in the ecosystem such as loss of biodiversity (Na, 2020).

Starting in the 19th century, catalysis was used as an alternative to mitigate and control fixed atmospheric emissions (Zanella, 2014). Its application for mobile sources was developed with the need to eliminate diesel engine gases through the SCR (Selective catalytic reduction) system with the injection of a reducing agent called urea (Wang, 2015) at 32% in water, functioning as an oxidant and combustion gas reducer (Decolatti, 2012). Currently, converters are composed of precious metals such as Platinum, Rhodium and Palladium, which behave as gas catalysts (Sen, 2016). On the other hand, these metals are highly expensive and present rapid deactivation, which has encouraged the use of zeolite, a mineral of the three-dimensional crystalline aluminosilicate type, with retention capacity, high selectivity and well-defined structures (Kianfar, 2020; Moliner and Corma, 2019).

The natural zeolite proved to be efficient in the conversion of CO for gasoline engines (Rajakrishnamoorthy et al., 2019), in reducing NO_x for diesel engines (Cho et al., 2017) and enhancement of tyre-derived oil quality (Namchot and Jitkarnka, 2015). Likewise, the ionic exchange of zeolite with metals improves its catalytic capacities and does not alter its morphology (Chen et al., 2018), which indicates that the metal species act as primary active sites (Lee et al., 2019), deducing that this catalyst is more active at low temperatures, because they present less CuO load (Pereda, 2014). As thermal support, ceramic monoliths are used, which are usually composed of cordierite in the form of honeycombs or foams, obtained by the extrusion and corrugation process (Govender and Friedrich, 2017). These are the most used in catalyst coating, due to their superior hydrothermal stability, low coefficient of thermal expansion and low cost (Wang, 2015).

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Although several studies have shown that zeolite is efficient and has retention capacity, this research makes it possible to contribute to the existing scientific knowledge on the use of Cu-Zeolite-based catalytic converters in old automobiles, as a potential alternative for the reduction of automobile emissions and accessible in economic terms and friendly with the environment. On the other hand, this study seeks to improve air quality and generate new ideas or knowledge of application in different industries, mobile sources and models.
For this reason, this study had as main objective to determine the reduction of the concentration of automotive internal combustion gases using CuZSM-5 (Zeolite Socony Movil) in a catalytic converter, under different operating and fuel conditions.

2. Materials and Methods

2.1 Synthesis and ion exchange of zeolite

The zeolite of the Pentasil type with Sodium (NaZSM-5) was synthesized by the hydrothermal method at pH 12. For this, 3.2 g of Sodium Hydroxide (NaOH) were dissolved in 269.14 mL of H_2O for 15 minutes, then 14.8 g of Tetrapropylammonium Bromide (TPABr), 3.4 g of Alumina (Al_2O_3) and 83.4 g of Colloidal Silica (SiO_2) were added under constant stirring for 15, 30 and 30 minutes, respectively. For hydrothermal crystallization, it was subjected to 120 °C for 72 h, and was subsequently washed, filtered, dried and calcined at 450 °C for 10 h. While, for ion exchange, a homogeneous mixture of the zeolite prepared with the 1M $CuSO_4$ solution was made in a 1: 5.4 weight to volume ratio (g: mL), the mixture was heated at 60 °C for 1 h, then it was stored for 48 h at room temperature. Finally, the final sample was washed with abundant distilled water and calcined at 400 °C (Guerrero, 2019).

2.2 Zeolite analysis

The thermal stability of the catalyst was examined by thermogravimetric analysis (Naffati et al., 2020), subjecting the NaZSM-5 sample to calcination for 10 h at 500 °C. The NaZSM-5 mass loss rate was calculated by the following equation:

$$\mathrm{w} = \frac{(\mathrm{m_f} - \mathrm{m_o})}{\mathrm{m_o}} \times 100\ \% \qquad (1)$$

Where, mo and mf represent the weight of the coated cordierite before and after calcination.

2.3 Monolith lining

The 400 CPSI honeycomb cordierite monolith was purchased by Ket Catalyst, Jiangsu, China. For the coating, a suspension of 8.1 g of CuZSM-5, 18 g of alumina, 19.3 g of binder and 550 mL of H_2O was prepared. Then, the cordierite monolith piece was immersed in the suspension, dried at 120 °C and calcined at 500 °C.

2.4 Manufacture of the catalytic converter

A catalytic converter with dimensions of 95 mm high, 147 mm long and 120 mm wide was manufactured (Figure 1). Next, the CuZSM-5 coated monolith was incorporated into the catalytic converter. The converter was then installed in the exhaust system of the 1984 Toyota Corona with a T3 Bi-fuel engine.

Figure 1: Converted Catalytic

2.5 Emissions test

The HC and CO emissions tests were performed before and after the installation of the catalytic converter, at four different speeds (idle, medium, high and very high) of 800, 1450, 2500 and 3250 revolutions per minute (rpm). The measurements were made with injection of LPG and gasoline, following the methodology of Supreme Decree Nro. 010-2017-MINAM. The percentage of reduction of HC and CO was calculated using the following equation:

$$\mathrm{w} = \frac{(\mathrm{C_o} - \mathrm{C_f})}{\mathrm{C_o}} \times 100\ \% \qquad (2)$$

Where, Co and Cf represent the concentrations of HC and CO before and after installing the converter.

3. Results and Discussion

3.1 Characteristics of the NaZSM-5 zeolite

Temperature is the most important operating factor in the operation of converters to achieve an effective removal of gases (Niu, 2017). Meanwhile, zeolite activates its catalyst source through temperature and reduces harmful gases into less harmful gases such as carbon dioxide (CO_2) or water vapor (H_2O). The thermogravimetric analysis of the NaZSM-5 zeolite is shown in Table 1.

Table 1: Thermal Stability of NaZSM-5 Zeolite

Calcination	Temperature (°C)	Time (h)	m_o (g)	m_f (g)	W (%)
NaZSM-5	500	10	7.8	7	11.4

The results of the TG analysis showed that the NaZSM-5 zeolite is stable under the conditions used during the heat treatment, with a minimum weight loss of 11.4%.
Regarding the composition and crystalline structure, previous studies show that the synthesis of CuZSM-5 presents a high dispersion of CuO in its structures (Trivedi and Prasad et al., 2018), which indicates a greater ion exchange capacity Sodium (Na) with Copper (Cu) (Yue et al., 2019) and a higher absorption of gases at low temperatures in that region (Wang et al., 2018). Furthermore, the surface area and the composition of the catalyst are not altered after the impregnation of copper in its structures, maintaining a composition similar to HZSM-5 (Chen et al., 2018).

3.2 CO emission analysis

The reduction of CO emission with and without the gasoline engine catalytic converter is shown in Figure 2

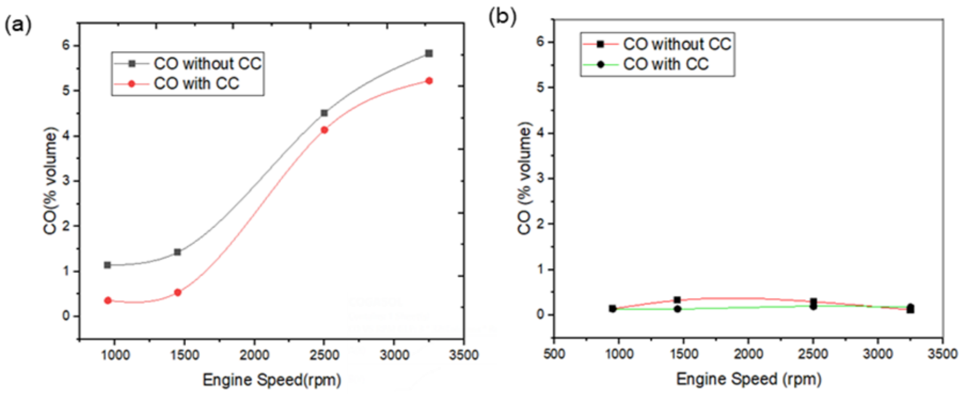

Figure 2: CO emission as a function of speed for (a) gasoline and (b) LPG engine

The results reveal that CO emissions increase with increasing engine speeds without a catalytic converter, while with a catalytic converter the concentration of CO decreases significantly due to the oxidation of CO from excess O2, as shown in equation 3 (Guerrero, 2019).

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + H_2 \quad (3)$$

For LPG consumption, CO emissions are lower than gasoline, because it has fewer carbon groups, are cleaner and have a high calorific value (Samaniego et al., 2016). Therefore, Figure 3 shows that the maximum concentration of CO was 0.33% vol. in average revolutions of 1500 rpm without catalyst, but with catalyst its concentration decreased to 0.14% vol. Proving that emissions are thus minimal, CuZSM-5 acts as an active source.

3.3 HC emission analysis

The influence of gasoline engine speed on HC emissions for both catalytic and non-catalytic configurations is shown in Figure 3a. The results reveal that HC emissions decrease with increasing engine speeds without catalyst, while with catalyst, the concentration drops significantly from 2000 rpm, reaching a minimum concentration of 261 ppm.

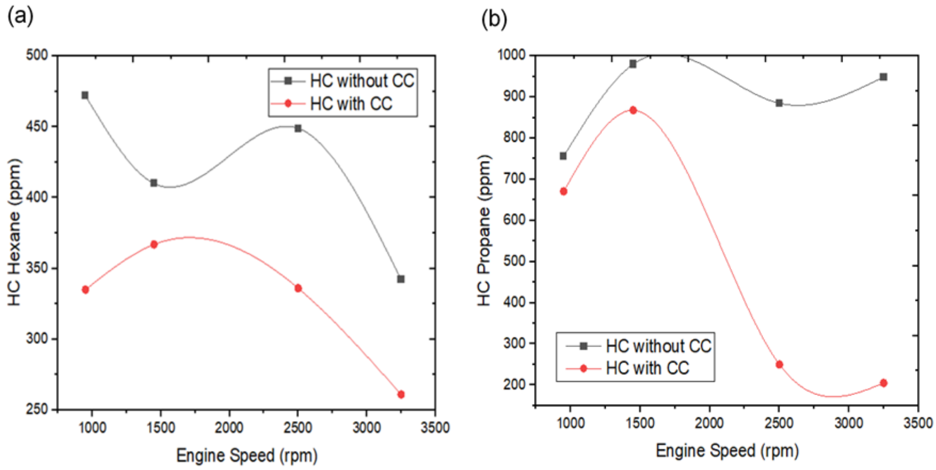

Figure 3: HC emission as a function of speed for (a) petrol engine and (b) LPG

Unlike CO, in this case the consumption of LPG generated a higher emission of unburned HC as shown in Figure 3b, with a maximum concentration of 980 ppm at 1500 rpm, while with catalytic configuration this emission began to decrease. significantly with the increase in engine speed reaching a maximum reduction of 205 ppm at 3250 rpm. This process is shown in equation 4 (Venkatesan, 2017).

$$C_xH_{2x} + 2 + \left[\frac{3x+1}{2}\right] O_2 \rightarrow xCO_2 + (x+1)H_2O \qquad (4)$$

The HC conversion is more efficient at high speeds, because it gives the engine more time to produce complete combustion and the converter to activate its catalytic source.

3.4 Catalytic efficiency

The reduction in CO concentration for a gasoline and LPG engine is shown in Figure 4a. The maximum CO reduction for gasoline engine was 68% at minimum speeds of 800 rpm and for LPG consumption, the maximum reduction was 60% at 1500 rpm, which indicates that CuZSM-5 zeolite can oxidize carbon monoxide. Carbon to carbon dioxide at minimum temperatures and speeds, as an effect of the reducing property of copper oxide that is concentrated in the zeolite structures. This effect was also observed by Ghofur (2018), which obtained a conversion of 45% of CO at 2000 rpm and Trivedi & Prasad (2018), with a conversion of 80% of CO at 1500 rpm. This behavior is closely related to the characteristics of CuZSM-5, due to the presence of copper oxide (CuO) in its crystalline structure, which helps to reduce CO at lower temperatures (Wang et al., 2018).

In other investigations, Heikens (2019) synthesized perovskite for its catalytic process and his X-ray diffraction analysis presented a high dispersion of PdO in its structure, which influenced the reduction of CO at high temperatures, while, Lee (2019) witnessed negative results when using an SSZ-13 type zeolite at low temperatures, which resulted in increased CO emissions. Confirming that CuZSM-5 has a unique behavior in reducing CO.

In the effective reduction of HC, a similar behavior was observed for both gasoline and LPG consumption; that is, the reduction of unburned HC increases with engine speed (Figure 4b). The maximum HC reduction for the gasoline engine was 29% at low revs and 24% at full revs. According to the results found by Baskara et al. (2018), who studied the CuZSM-5 and obtained a 45% reduction at 1600 rpm. On the other hand, for LPG consumption the maximum reduction of HC was 78% at high revolutions. During this process, the HC is oxidized to H_2O and CO_2 due to the effect of excess oxygen or other reactions, this effect was also observed by Karthe et al. (2016) and Karthikeyan et al. (2016), who managed to reduce HC by 80% using CuZSM-5 under the same conditions.

The coating of the 400 CPSI cordierite with 20 g of catalyst suspension had a positive influence on the reduction of HC and CO emission. This effect was also observed by Rajakrishnamorthy (2019), when he used a dose of 16% coating and obtained positive results such as a 65% reduction of gases at 180 °C. On the other hand, the excess dose causes a saturation of pores, reducing the reducing capacity of the catalyst (Zamaro et al., 2005).

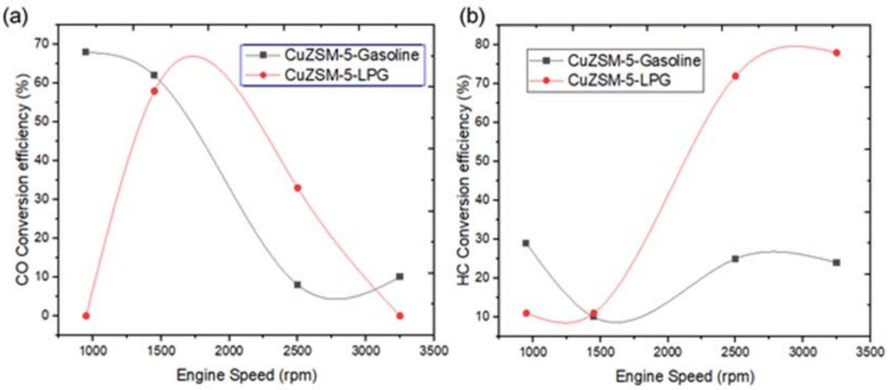

Figure 4: (a) CO reduction as a function of speed and (b) HC reduction as a function of speed

4. Conclusions

The use of the catalyst (CuZSM-5) inside the catalytic converter was favourable, economically profitable and efficient in reducing automotive gases. The results indicated that the incorporation of copper over NaZSM-5 zeolite strongly promoted the reduction of CO emission by 68% at minimum speeds of 800 rpm for a gasoline engine and 78% for HC Propane at high speeds of 2750 rpm for a LPG engine, indicating that the coating load of 20 g of CuZSM-5 positively influenced the reduction of automotive internal combustion gases, since no clogging of pores and negative reduction results were observed. Moreover, CuZSM-5 presented thermal stability and removal capacity of HC and CO, which would be related to the dispersion of CuO particles in its structure, which act as catalyst sources. It is reasonable to conclude that CuZSM-5 attached to cordierite has the ability to reduce automobile emissions from the combustion of different fuels such as LPG and gasoline.

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