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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Copper-Exchanged Philippine Natural Zeolite as Potential Alternative to Noble Metal Catalysts in Three-Way Catalytic Converters

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Abstract

Natural and synthetic zeolites are microporous hydrated aluminosilicate minerals known for their high thermal stability and their use in various catalytic applications. In this study, the potential of modified Philippine natural zeolite as a cheap alternative to noble metal catalysts in three-way catalytic converters was investigated. The natural zeolite (Z) of the heulandite variety was treated using hydrochloric acid and then ion-exchanged with sodium (NaZ) and copper (CuZ) ions in succession. Energy-dispersive X-ray spectroscopy analysis revealed successful replacement of sodium and other exchangeable cations by copper in the zeolite at 1.19%. Morphological features using scanning electron microscope have shown uniform dispersion of copper as well as uniform particle distribution. In the emission study, a stationary two-stroke 125 cm^3 spark-ignition gasoline engine motorcycle at three different speeds of 10 (low), 40 (medium) and 70 (high) kilometers per hour (kph) was used to investigate the catalytic properties of CuZ with the non-catalytic setup as baseline. Using the modified zeolite catalyst, emission test results have shown significant reduction in carbon monoxide (CO) and hydrocarbon (HC) emissions in all speeds, while nitrogen monoxide (NO) emission was significantly reduced from medium to high speeds, suggesting that NO reduction was highly influenced by reaction temperature. Highest reduction in CO emission was 59.61% at medium speed, while highest HC and NO emissions were 66.52% and 76.63%, respectively, at high speed. While further tests are recommended, results show the potential of modified Philippine natural zeolite as a cheap alternative material for three-way catalytic converters.

Keywords Zeolite · Catalysis · Emission · Air pollution · Copper · Automotive

Abbreviations

Z	Philippine natural zeolite
HZ	Hydrochloric acid-treated Philippine natural zeolite
NaZ	Sodium-exchanged Philippine natural zeolite
CuZ	Copper-exchanged Philippine natural zeolite
EDS	Energy-dispersive X-ray spectroscopy
XRD	X-ray diffraction spectroscopy
XRF	X-ray fluorescence spectroscopy
SAR	Silica–alumina ratio
SEM	Scanning electron microscope
SI	Spark-ignition engine
HCl	Hydrochloric acid
CO	Carbon monoxide
HC	Hydrocarbons
NO	Nitrogen monoxide
kph	Kilometers per hour
catcon	Catalytic converter

1 Introduction

Each year, million metric tons of air pollutants is released worldwide and a significant part of these emissions come from on-road vehicles [1–3]. Combustion of fossil fuels in automotive internal combustion engines produces many harmful products such as unburned and partially burned hydrocarbons (HC), carbon monoxide (CO) and nitrogen

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oxides (NO_x). These chemicals have adverse effects to human health, and some are even precursors to other pollutants like tropospheric ozone, acid rain and photochemical smog. To lessen the impact of vehicular emissions on health and the environment, three-way catalytic converters (catcon) were developed. Catalysts inside a three-way catalytic converter help in the oxidation and reduction (redox) processes to lower the concentration of harmful combustion products released to air. The CO and HC emissions, for example, are oxidized to CO_2, including water for the case of HC, while NO_x is reduced to N_2 and O_2 gases [4–6]. Catalytic converters are usually made from ceramic materials coated with precious metals such as platinum, palladium and rhodium which initiate the catalytic redox reactions [7]. However, these metals are expensive and in limited supply [8] and the increase in their anthropogenic emission is associated with some health problems [9].

Zeolites, on the other hand, have been used in various catalytic applications with a wide operating temperature range as well as high thermal stability [10]. They are microporous hydrated aluminosilicate minerals with highly ordered channel structure and can be natural or synthetic in nature. These characteristics have attracted interest among researchers to develop robust and efficient but cheaper alternative to conventional catalytic converters. One study demonstrated that by coating copper and silver in 13-X zeolite can reduce NO_x and oxidize CO and HC emissions in a petrol engine [11], while metal-containing ZSM-5 zeolites have been studied for the catalytic reduction of NO_x with hydrocarbons [12]. More recently, copper- and iron-exchanged NaX zeolites have been used in a twin-cylinder nano-engine and have shown CO and HC emission reduction efficiencies at par with a commercial catalytic converter while having exceptional NO_x conversion efficiency [13]. Other studies using ion-exchanged X zeolites have also shown positive results when using them as catalysts for spark-ignition (SI) engine emission control [4, 14].

While several studies demonstrated the ability of zeolites as potential alternative to conventional catalytic converters, these studies utilize synthetic types which can still be limiting in terms of cost. On the other hand, other research studies using the cheaper natural zeolites as alternative catalysts for engine exhaust applications still remain limited. In one study, ammonium-treated and cobalt-modified clinoptilolite successfully decreased the content of nitrogen oxides in exhaust gases even during cold start [15], while cobalt- and rhodium-modified natural zeolites (clinoptilolite and clinoptilolite–mordenite) were successfully demonstrated to oxidize propane and naphthalene with a 100% conversion at 250 °C [16]. Furthermore, copper oxide supported on matrixes from Jordanian natural zeolite, Syrian bentonite and alumina were used in the removal of NO_x, HC and CO emitted from car exhaust flow controlled by a micro-pulse-like reactor achieving more than 50% removal for HC and CO and up to 41% reduction for NO_x [17].

In this work, a low-cost Philippine natural zeolite of the heulandite variety was chemically treated and modified by ion exchange method to investigate its applicability as a low-cost alternative to commercial three-way catalytic converters. Copper was chosen as the metal catalyst for the ion exchange process due to its ability to reduce emissions as described by previous studies [4, 5, 11, 13] along with its availability and relatively low cost. A catcon enclosure was designed and fabricated, and the emission reduction performance of the modified Philippine natural zeolite was demonstrated using a stationary 125 cm^3 spark-ignition gasoline motorcycle engine at different speeds.

2 Experimental

2.1 Zeolite Treatment and Ion Exchange

Philippine natural zeolite (Z) granules from Saile Industries, Pangasinan, the Philippines, were washed with deionized (DI) water in 1:5 weight ratio (zeolite:water) to remove residual fine particles and dried at 150 °C for 1 h. Subsequently, samples were soaked in 3 M (molar) concentration (about 10 wt %) hydrochloric acid (HCl) solution in 1:5 weight ratio for 12 h [18], washed with DI water until neutral pH to remove the Cl^- ions and then dried at 150 °C for 6 h. To prepare for ion exchange, the HCl-treated zeolite samples (HZ) were immersed in 4 M NaCl solution in 1:5 weight ratio for 24 h to incorporate Na^+ ion in the zeolite [19]. The sodium-exchanged zeolite (NaZ) samples were then washed and dried at 150 °C for 6 h. The copper ion exchange process was carried out by homogenously mixing NaZ with 1 M CuSO4 solution in 1:5.4 weight-to-volume (g:mL) ratio at 60 °C for 1 h and then allowed to soak further for 24 h. After soaking, the copper-exchanged zeolite (CuZ) samples were then washed once with DI water and calcined for 4 h at 400 °C.

2.2 Characterization of Zeolite Samples

The X-ray diffraction (XRD) for zeolite sample, Z and energy-dispersive X-ray fluorescence spectroscopy (XRF) analyses for samples Z, HZ and NaZ were conducted at the University of the Philippines—National Institute of Geological Sciences. For morphology and copper uptake, scanning electron microscopy with energy-dispersive X-ray (SEM–EDS) analyses on NaZ and CuZ samples was performed using JEOL-5300 at the Science and Technology Research Center of De La Salle University—Manila.

Table 1 Engine specifications

Specification	Details
Engine model	Kawasaki HD3
Engine type	Two-stroke, single-cylinder rotary disk valve
Displacement	125 cubic centimeter
Bore and stroke	55 mm × 52.5 mm
Compression ratio	6.4:1
Maximum power	13 horsepower @ 6500 rpm
Maximum torque	1.45 kg-m @ 5000 rpm

2.3 Emission Testing

A catalytic converter housing or enclosure was designed based on the Bersy OSCA model [20] and fabricated using galvanized iron sheets for the outer casing and aluminum sheets and screens for the internal compartment. The emission test was carried out using a stationary two-stroke Kawasaki HD3 125 cm^3 spark-ignition gasoline engine motorcycle with specifications shown in Table 1 and loaded with 95 octane rating gasoline.

Exhaust gas emissions were measured for catalytic and non-catalytic setup at three different speeds of 10 (low), 40 (medium) and 70 (high) kilometers per hour (kph). The non-catalytic setup was used as a baseline for the percent reduction calculations. The concentration of exhaust carbon monoxide (CO), hydrocarbon (HC) and nitrogen monoxide (NO) was determined using the FGA-4100(5G) automotive emission analyzer with specifications shown in Table 2. The emission test procedure used was obtained from the Department of Environment and Natural Resources Administrative Order Number 23 Series of 2010 (DAO 2010-23) Annex A [21] and conducted in a Land Transportation Office (LTO)-certified emission testing center in Pilar, Bataan, the Philippines.

3 Results and Discussion

3.1 Characterization of Zeolite Samples

From a previous study [22] by one of the authors, the natural zeolite sample (Z) from Saile Industries, Inc., showed that the principal component was from the heulandite variety with some presence of mordenite and clinoptilolite minerals as shown by the XRD peaks in Fig. 1.

To improve adsorption characteristics of the natural zeolite, acid treatment was performed by removing impurities that block the porous channels. Acid treatment progressively eliminated intrinsic cations such as calcium (Ca), magnesium (Mg) and iron (Fe) which transformed the zeolite to its H form (HZ), and finally dealuminated the structure as seen from the XRF results in Table 3. The acid treatment made some significant changes in the zeolite particularly in the reduction of aluminum from 12.34% in Z to 9.64% by weight in HZ as well as reduction of Ca, Mg, Fe, K and Mn. The removal of alumina in the zeolite caused enlargement of pore sizes in both the main channels and side pockets [23]. On the other hand, Si composition increased significantly from 60.43 to 72.09 wt%, causing an increase in the Si/Al ratio (SAR). The SAR for Z and HZ samples were 4.897

Table 2 Automotive emission analyzer specifications

Model		FGA-4100 (5G)
Measuring ranges		
HC		$(0–9.999) \times 10^{-6}$ vol
CO		$(0–10) \times 10^{-2}$ vol
CO_2		$(0–20) \times 10^{-2}$ vol
O_2		$(0–25) \times 10^{-2}$ vol
NO		$(0–5000) \times 10^{-6}$ vol
λ		0.5–3.0
Oil temperature		(0–150)°C
Speed		(0–10,000) rev/min
	Absolute error	Relative error
Indication error		
HC	$\pm 12 \times 10^{-6}$ vol	± 5%
CO	$\pm 0.06 \times 10^{-2}$ vol	± 5%
CO_2	$\pm 0.5 \times 10^{-2}$ vol	± 5%
O_2	$\pm 0.1 \times 10^{-2}$ vol	± 5%
NO	$\pm 25 \times 10^{-6}$ vol	± 4%
Response time	$HC/CO/CO_2$: ≤ 8 s: O_2/NO: ≤ 12 s	
Power	AC (220 V ± 22) V; (50 ± 1) Hz	
Output interface	RS-232/RS-485	
Weight	Approximately 9 kg	
Dimension	310 mm × 170 mm × 400 mm	

HC hydrocarbon, λ excessive air coefficient

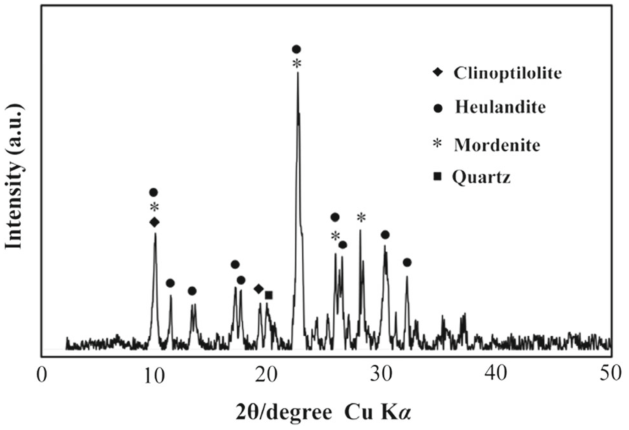


Fig. 1 XRD pattern of Philippine natural zeolite [22]

and 7.478, respectively. The framework Si/Al ratio of zeolites is an important parameter which strongly influences ion exchange capacity. Generally, zeolites with low aluminum content or high SAR are more favorable when applied as catalysts [24]. In preparation for copper cation exchange, sodium ion was successfully incorporated in HZ with about 1.24% Na in the zeolite (Table 3). The Na^+ ion is the most weakly bound ion in the zeolite and can be exchanged easily with other cations in solution.

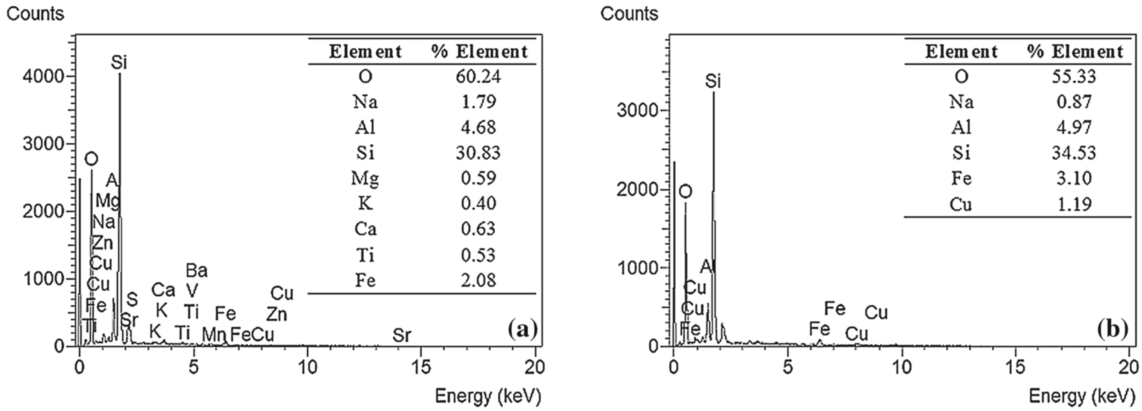
Table 3 Chemical composition (% mass) of zeolite samples by XRF (note: minor elements are removed)

Element	Z	HZ	NaZ
Al	12.34	9.64	10.46
Ca	11.19	3.94	3.37
Fe	11.22	10.58	10.84
K	1.73	1.35	1.43
Mg	1.13	0.71	0.89
Mn	0.29	0.19	0.20
Na	–	–	1.24
Si	60.43	72.09	69.63
Sr	0.30	0.12	0.13
Ti	1.26	1.31	1.36

3.2 SEM–EDS Analyses of Cation-Exchanged Zeolites

The EDS spectra of NaZ and CuZ are shown in Fig. 2a, b, respectively, which indicated successful replacement of sodium by copper ions. Peaks of Na at 1.04 keV and Ca at 3.69 keV were observed in the NaZ spectrum (Fig. 2a), but their peak intensities diminished after ion exchange (Fig. 2b). This suggests that exchangeable cations from NaZ such as Na^+ and Ca^{2+} ions have been replaced by Cu^{2+} ions as supported by the occurrence of Cu peak at 8.04 keV (Fig. 2b). The aluminosilicate nature of the zeolite was also confirmed from both NaZ and CuZ spectra as shown by the high peak intensities of Si, Al and O with CuZ containing about 1.19% Cu by weight (Fig. 2b). The copper contained in the zeolite will provide the catalytic function needed for the reduction of harmful air pollutants such as CO, HC and NO released from engine combustion [4, 5, 10, 11, 13].

SEM micrographs of NaZ and CuZ are shown in Fig. 3a, b, respectively. Surface morphology suggests NaZ and CuZ were not considerably different. This is an indication that no



Element	% Element
O	60.24
Na	1.79
Al	4.68
Si	30.83
Mg	0.59
K	0.40
Ca	0.63
Ti	0.53
Fe	2.08

Element	% Element
O	55.33
Na	0.87
Al	4.97
Si	34.53
Fe	3.10
Cu	1.19

Fig. 2 EDS spectra of **a** NaZ and **b** CuZ samples (note: the % composition was included with some minor elements removed)

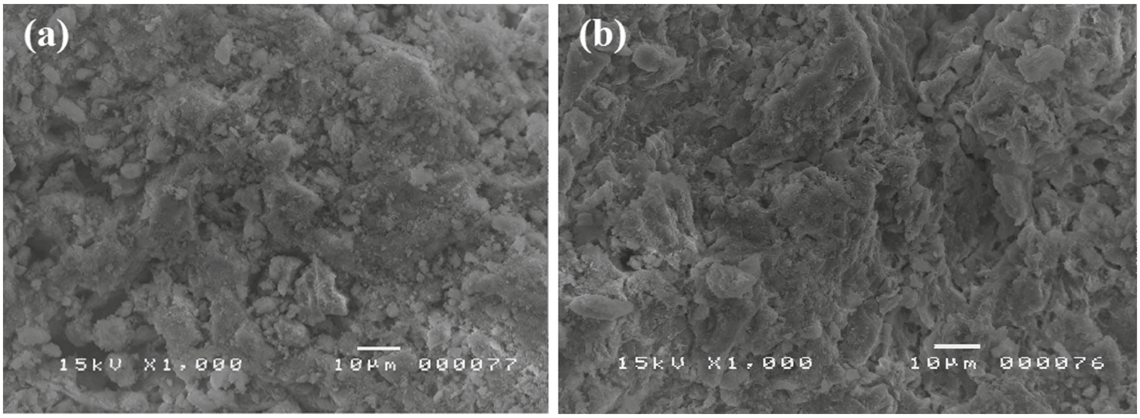


Fig. 3 SEM images of **a** NaZ and **b** CuZ samples

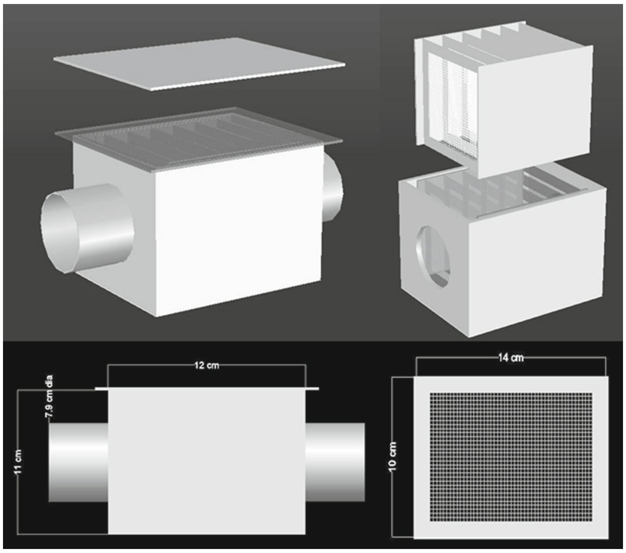


Fig. 4 Design and dimensions of catcon enclosure

Cu^{+2} ions inside the zeolite were in discrete phase, manifesting high dispersion of the copper cations. Moreover, it was observed in the surface micrograph that CuZ had well-distributed particles with a large surface area attributed to the rough surface and micro-pore structures (Fig. 3b).

3.3 Effect of Engine Speed to CO, HC and NO Emissions

For the purpose of simplification, the sizing design of the catalytic converter enclosure was based on the Bersy OSCA V3NA model [20] which considers the type and volumetric capacity of the engine. With these considerations, an enclosure illustrated in Fig. 4 with dimensions of 10 cm by 14 cm by 10 cm (L × W × H) with inlet and outlet pipe diameters of 7.9 cm was fabricated using the materials described earlier.

The actual image of the catcon enclosure containing the natural zeolites in granular form is shown in Fig. 5. Prior to emission test, a 4-inch aluminum flexible tube was connected from the muffler of the spark-ignition (SI) engine to the inlet pipe of the catalytic converter enclosure using aluminum tape. Pollutant concentrations were recorded and reported as averaged values once they have stabilized during the emission tests.

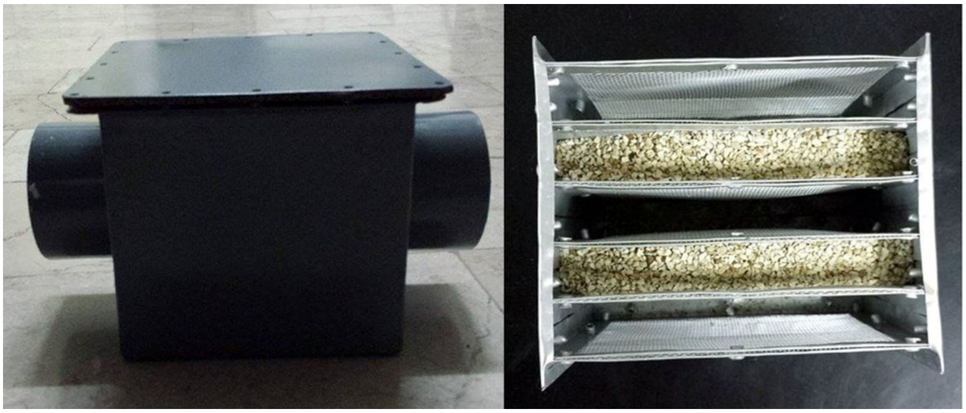
The effect of engine speed on HC and NO emissions for both catalytic and non-catalytic setups is shown in Fig. 6 with concentration values reported as parts per million (ppm) volume. Results reveal that HC emissions increased with increasing engine speeds for the non-catalytic setup, while the catcon setup was not significantly affected. In fact, a slight improvement in the HC emission was observed when engine reached medium to high speeds. The increase in unburned HC emission is influenced by faster fuel injection when the engine runs at higher speeds leading to insufficient time for complete combustion to take place. However, a significant reduction of HC was achieved when CuZ was used as a catalyst when compared to the non-catalytic setup. Decrease in HC emissions is attributed to the oxidizing ability of copper which utilizes excess oxygen from the exhaust gases as described by previous studies [5, 6] and represented by Eq. 1 [25]. During this conversion process, HC is oxidized to H_2O and CO_2 [5, 6], while other reaction may occur inside the catalytic converter such as steam reforming as shown by Eq. 2 [26]. In terms of percentage reduction, highest HC reduction was achieved by CuZ at 66.52% at high speed.

$$C_yH_n + \left(1 + \frac{n}{4}\right)O_2 \xrightarrow{\text{catalyst}} yCO_2 + \frac{n}{2}H_2O \tag{1}$$

$$HC + H_2O \xrightarrow{\text{catalyst}} CO_2 + H_2 \tag{2}$$

For the NO emission, similar behavior was observed for both catalytic and non-catalytic setups; that is, NO emission increased when engine speed increases (Fig. 6). Nitrogen oxides form because of high-temperature conditions during combustion [4], and increasing engine speeds further promote this type of condition. For the CuZ catalyst, the NO reduction activity was observed particularly at medium to

Fig. 5 Actual image of catcon enclosure containing natural zeolites



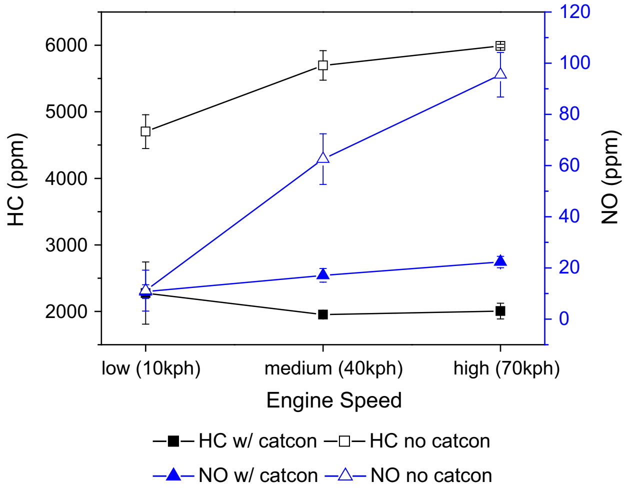


Fig. 6 HC and NO_x emissions against engine speed

high engine speeds. The NO reduction was minimal at low engine speed in the catcon setup possibly due to the absence of desired temperature that the catalyst needed in order for the reaction process to proceed. Certain temperature conditions are also necessary to initiate catalytic activity such as in the case of NO reduction [4] which was only achieved from medium to high speeds in this study. To further support this, NO emission over time is plotted in Fig. 7. The graph shows that significant NO reduction using CuZ as catalyst was achieved only after 30 s or just when the speed was adjusted to 40 kph or at medium speed. This implies that catalytic activity is indeed initiated at higher speed and temperature. Moreover, it was also observed that further increasing the speed to 70 kph or high speed did not translate to a significant increase in NO emission unlike that of the non-catalytic setup. This behavior suggests stability of the catalyst even at extreme engine conditions as long as the desired temperature is achieved. However, further tests are suggested in order to determine the specific temperature or the light-off temperature by which the catalytic reactions are initiated and other operating parameters needed for optimal catalyst configuration. NO reduction processes convert the compound to N_2 and O_2 gases [4] with the presence of other combustion gases such as CO and HC and aided by the catalyst. These reduction reactions are represented by Eqs. 3, 4 and 5 [25]. Maximum reduction for NO at 76.63% was also achieved at high engine speed.

$$\mathrm{NO}(\text{or } \mathrm{NO}_2) + \mathrm{CO} \xrightarrow{\text{catalyst}} \frac{1}{2}\mathrm{N}_2 + \mathrm{CO}_2 \tag{3}$$

$$\mathrm{NO}(\text{or } \mathrm{NO}_2) + \mathrm{H}_2 \xrightarrow{\text{catalyst}} \frac{1}{2}\mathrm{N}_2 + \mathrm{H}_2\mathrm{O} \tag{4}$$

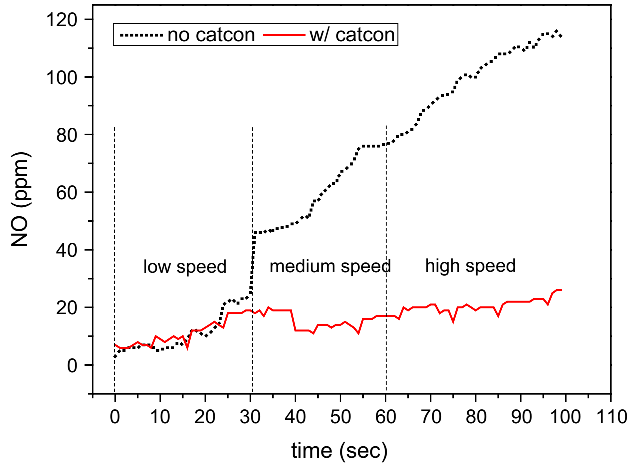


Fig. 7 NO emission over time

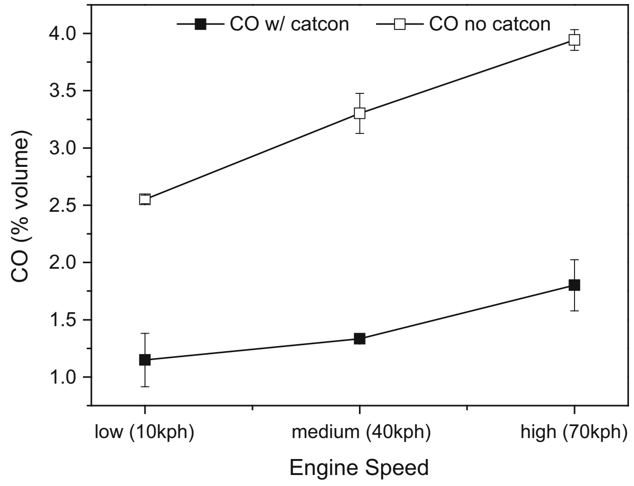


Fig. 8 CO emission against engine speed

$$\left(2+\frac{n}{2}\right)\mathrm{NO}\,(\text{or } \mathrm{NO}_2) + C_yH_n \xrightarrow{\text{catalyst}} \left(1+\frac{n}{4}\right)\mathrm{N}_2 + y\mathrm{CO}_2 + \frac{n}{2}\mathrm{H}_2\mathrm{O} \tag{5}$$

The effect of engine speed on CO emission for both catalytic and non-catalytic setups is shown in Fig. 8 with concentration values reported as percentage by volume (% volume). For both setups, CO emission concentration increased as engine speed increases though CO emission in the catalytic setup was much less significant as shown in Fig. 8. Higher engine speeds require faster fuel injection which translates to shorter combustion time, leading to incomplete combustion. As a result, higher CO emission was observed for both setups at higher engine speeds with significant increase in the non-catalytic setup. On the other hand, the catalytic activity of CuZ was again successfully demonstrated as shown by significant reduction in CO emissions

Table 4 Summary of % reduction in HC, NO and CO emissions at different engine speeds

Engine speed	HC emission (ppm)			NO emission (ppm)			CO emission (% volume)		
	w/o catcon	With catcon	% reduction	w/o catcon	With catcon	% reduction	w/o catcon	With catcon	% reduction
Low (10 kph)	4702 ± 254	2276 ± 466	51.60	11.1 ± 8.0	10.7 ± 2.7	3.84	11.1 ± 2.6	10.7 ± 2.7	54.96
Medium (40 kph)	5698 ± 222	1951 ± 34	65.76	62.5 ± 9.9	17.1 ± 2.7	72.65	62.5 ± 3.3	17.1 ± 2.7	59.61
High (70 kph)	5988 ± 26	2005 ± 118	66.52	95.5 ± 8.7	22.3 ± 2.2	76.63	95.5 ± 3.9	22.3 ± 2.2	54.32

compared to the non-catalytic setup. Similar to HC oxidation process, CuZ was able to oxidize CO to CO_2 using the excess O_2 from the exhaust and as described by other studies using copper as catalyst [5, 6]. The CO oxidation from excess O_2 and other oxidation reaction such as the water gas shift reaction occurring during combustion in the presence of a catalyst are represented by Eqs. 6 and 7, respectively [26]. Highest reduction in CO emission was achieved at 59.61% at medium speed.

$$CO + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} CO_2 + H_2 \tag{6}$$

$$CO + H_2O \xrightarrow{\text{catalyst}} CO_2 + H_2 \tag{7}$$

The % reduction in HC, NO and CO emissions at different engine speeds is summarized in Table 4. It was observed that with increasing speed, percent reduction in HC and NO emissions also increased, while CO emission was not significantly affected for the catalytic setup.

4 Conclusions

This work has demonstrated that the modification of Philippine natural zeolite via copper cation exchange process as an alternative material for three-way catalytic converters can be successfully developed for 125 cm^3 spark-ignition engine. Results show that copper-exchanged zeolite can act as catalyst for both oxidation and reduction of air pollutants. For a non-catalytic engine setup, increasing engine speed increased CO, HC and NO emissions. However, the presence of the modified zeolite catalyst was able to minimize or control this behavior. Compared to the non-catalytic setup, significant reduction for HC and CO was achieved at all engine speeds, while significant NO reduction occurred at medium to high speeds, suggesting that NO conversion was highly influenced by reaction temperature. It was observed that with increasing speed, percent reduction in HC and NO emissions also increased, while CO emission was not significantly affected for the catalytic setup. The highest reduction in HC and NO emissions was achieved at high speed at 66.51% and 76.63%, respectively. On the other hand, highest CO reduction at 59.61% using CuZ as catalyst occurred at medium speed. While further tests are recommended for optimal configuration and commercial acceptability, results show the potential of modified Philippine natural zeolite as a low-cost but effective alternative material for three-way catalytic converters.

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