Journal of Applied Science & Process Engineering
Vol. 7, No. 1, 2020

Passive Nitrogen Oxides Removal from a Diesel-engine Exhaust Gas Using a Biomass-carbon Catalyst

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Abstract

Nitrogen oxides (NO_x) removal from a diesel-engine exhaust gas requires the utilization of ammonia/urea as a reducing agent (SCR) which arose environmental concerns over the use of this chemical. Therefore, this study explored the potential of using a sustainable NO_x removal system by replacing ammonia with intrinsic reductants present in the exhaust gas, such as hydrocarbons and carbon monoxide, and by application of cost-effective carbon-supported transitional metals catalyst. Copper-cerium catalyst supported over palm kernel shell activated carbon (Cu-Ce/PKS) was synthesized via deposition-precipitation method. The characterization shows that the catalyst has a considerably high surface area (though lower than the support). The high NO_x removal by Cu-Ce/PKS in a passive catalytic reaction is attributable to the surface area provided by the carbon support, the low copper reducibility which leads to the low optimum operating temperature, and the synergistic effect between Cu and Ce which resulted in the wide temperature window at low-temperature range. It is concluded that Cu-Ce supported over palm kernel shell activated carbon can be further developed to reduce NO_x in a passive catalytic removal for a sustainable and cost-effective SCR system.

Keywords: *NO_x removal, Passive catalytic reduction, Carbon-supported catalyst, Deposition-precipitation method, Synergistic effect*

1. Introduction

Nitrogen oxides (NO_x) emitted from combustion/incineration processes typically consist of 95 % nitric oxide (NO) and 5 % nitrogen dioxide (NO_2), where NO is considered as the most difficult compound to remove from ambient air for it is nearly insoluble in water [1] [2]. Ammonia-selective catalytic reduction (SCR) is a commonly used technique to remove this toxic gas from an exhaust/flue gas emission. However, a phenomenon called ammonia slip, where the unreacted ammonia is also emitted in the exhaust gas prompted studies on the ammonia replacement as a reducing agent. Among the attractive methods to reduce NO_x emissions from the combustion flue gas is selective catalytic reduction with hydrocarbons (HC-SCR) and/or carbon monoxide (CO-SCR). It is known that both HC and CO are present in a diesel engine exhaust gas due to the incomplete combustion of the fuel. By utilizing the intrinsic carbon monoxide and unburned hydrocarbons to replace ammonia as a reductant in SCR, the cost of NO_x removal can be reduced because of the elimination of ammonia/urea injection

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Manuscript History:
Received 16 April, 2020, Revised 28 April, 2020, Accepted 29 April, 2020, Published 30 April, 2020

system [3]. There are two modes of SCR: the usage of the intrinsic HC and CO in the exhaust gas, known as the passive mode; and by injecting additional HC and/or CO, which is called the active mode – the former being the interest of this research study [4].

Copper and cerium are among the most commonly studied transitional metal catalysts in SCR. Both of these metals have lower costs as compared to precious metals and typically have a higher resistance to sulphur compounds, water poisoning, and carbon dioxide [5]. Copper is known to exhibit high activity which is enhanced by the presence of oxygen, while cerium has been widely used as an active species or an additive because of its unique redox and acid-base properties [6] [7]. It was reported that cerium oxide enhanced the oxidation of NO to NO_2, leading to an enhanced SCR activity [7] [8]. With these advantages, Cu and Ce could be considered as excellent catalysts for a passive SCR.

Activated carbon (AC) is a black and amorphous solid containing a major portion of fixed carbon content, volatile matters and ash. Due to its large internal pore structures and pore volume, AC has a high adsorbing capacity for most compounds. This highly developed porous structure has resulted from the processing of carbonaceous raw materials under high-temperature reactions [9]. Besides acting as an adsorbent, activated carbon can also be applied as a catalyst and catalyst support to metal oxide catalysts. This is because, in addition to porosity, surface chemistry of the carbon is also contributing to the catalyst reactivity [10].

Palm kernel shell (PKS) has been one of the most promising precursors for the production of high-grade activated carbon as it has high density, high carbon content and low ash properties [11]. In Malaysia, there is a high potential for the application and production of activated carbon using PKS. The production of oil palm fresh fruit bunch (FFB) saw an increment from 48 million to 70 million from 2000 to 2012, and an additional of 315,306 ha of oil palm (6 % increase from 2012) were planted since then [12] [13]. This showed positive growth in the future years for the plantation, and PKS will also increase as each tonne of FFB produces approximately 55 kg of PKS [13]. Because most of the portions were under-utilized, PKS can be used as a sustainable raw material for the activated carbon production. Biomass waste utilization is relatively economical because it is sourced from agricultural wastes which are readily available. Therefore, activated carbon from biomass waste has a lower capital cost and is favoured in the application of removing NO_x gases [14]. Considering the state-of-the-art of the passive SCR and the advantages of using PKS, the aim of this study is to investigate the performance of PKS-supported Cu-Ce catalyst in a passive catalytic removal of NO_x gases.

2. Materials and method

2.1. Catalyst synthesis

Activated carbon derived from palm kernel shell was obtained from a local supplier and dried in a laboratory oven overnight at 110 °C. The catalysts were prepared by using the deposition-precipitation method with urea as the precipitating agent. 50 g of activated carbon was weighed, and metal salts (copper and cerium) were dissolved using deionized water in a separate beaker. The Cu:Ce ratio was 1:1 for the bimetallic Cu-Ce/PKS with 10 wt% total loading, and the loading was kept constant for the monometallic catalysts Cu/PKS and Ce/PKS. The metal solutions were mixed with the activated carbon and stirred well for 15 mins before 15 mL of 1 M urea solution was poured into the mixture and stirred at 90 °C for 6 h. Subsequently, the slurry was filtered to remove the excess solution, washed until it was clear, and dried at 110 °C in an oven overnight, followed by calcination at 250 °C for 4 h in a furnace.

2.2. Passive NO_x catalytic removal

The catalytic activity was studied at a temperature between 140 and 300 °C with 40 °C interval. An air-cooled 4-stroke single-cylinder diesel engine of at least 3000 rpm was used in this experiment. The exhaust from this engine was connected to a filter to remove soot and liquid effluent before entering a catalytic bed of 20 mm inner diameter. Testo 350 XL Flue Gas Analyser (Germany) was used to measure the concentration of NO_x before and after the reactor. 10 g of the catalyst was placed inside the reactor and heated to the desired temperature. Then, the valve connecting the exhaust and the reactor was turned on. The flow rate of flue gas was fixed to 1 L/min giving 3000 h^{-1} GHSV. No external source of hydrocarbon or carbon monoxide was injected to resemble the passive mode of this system. No repetition was made to avoid the excessive release of toxic NO_x. The experiment was carried out until equilibrium NO_x concentration was obtained and was performed for different catalysts; PKS, Cu/PKS, Ce/PKS and Cu-Ce/PKS respectively.

2.3. Catalyst characterization

The carbon support (PKS), the monometallic catalysts (Cu/PKS and Ce/PKS) and the bimetallic catalyst (Cu-Ce/PKS) were characterized to determine the contribution of each of the elements (carbon support, Cu and Ce) on the performance of Cu-Ce/PKS. The Brunauer-Emmet-Teller (BET) surface area was determined via a nitrogen adsorption-desorption experiment, the presence of the surface functional groups was observed using Fourier-Transform Infra-Red (FTIR), the distribution of copper and cerium particles on the catalyst was perceived from an energy dispersive X-ray fluorescence (XRF), and the reducibility of the catalysts was determined by a temperature-programmed reduction (TPR).

0.2 to 0.3 g of the sample was placed into a quartz U-tube and contacted with nitrogen gas at a relative pressure (P/P_0) of up to 1.00. Nitrogen adsorption-desorption was measured using Autosorb iQ Automated Gas Sorption (USA) at liquid nitrogen temperature (-196 °C). BET method was used to calculate the specific surface area and pore volume. 0.1 g of the sample was mixed with 1.0 g of KBr and pressed to become a solid disc. The disc was then placed in an oven at 105 °C for 4 h to prevent any interference with water vapour molecules. The analysis was performed by using a Thermo Nicolet 380 (USA) with the wavelength ranging from 400 to 4000 cm^{-1}. The change in the FTIR spectra was observed after deposition with catalysts showing the effects on the surface functional groups.

The sample (about 0.1 g) was crushed into powder form and placed on a stub in an EDX-720/800HS Energy Dispersive X-ray Fluorescence (Japan). It was exposed to X-ray radiation, and a set of energy released corresponds to a specific type of inorganic matter present in the sample. The standard deviation for the composition represents the distribution of the metal over the material surfaces. The most efficient reduction temperature for the impregnated catalyst was studied by using a hydrogen temperature-programmed reduction (TPR). This analysis was performed using a Thermo Finnigan TPDRO 1100 (USA), where approximately 20 mg of the sample was reduced under a 5 % hydrogen gas at 10 °C/min until 950 °C. The area under the TPR curve represents the amount of hydrogen being consumed by the sample reflecting the reduction activity at a particular temperature.

3. Results and discussion

3.1. Performance of Cu-Ce bimetallic catalyst in a passive NO_x removal

The activity of Cu-Ce/PKS in removing NO_x gases was evaluated in a passive SCR mode, and the results are shown in Figure 1. The catalyst exhibited increased removal percentage at low temperature but not at high temperature as compared to the raw PKS and the monometallic catalysts.

However, on overall, Cu-Ce/PKS gave the highest NO_x removal percentage with 66 % removal at 140 °C.

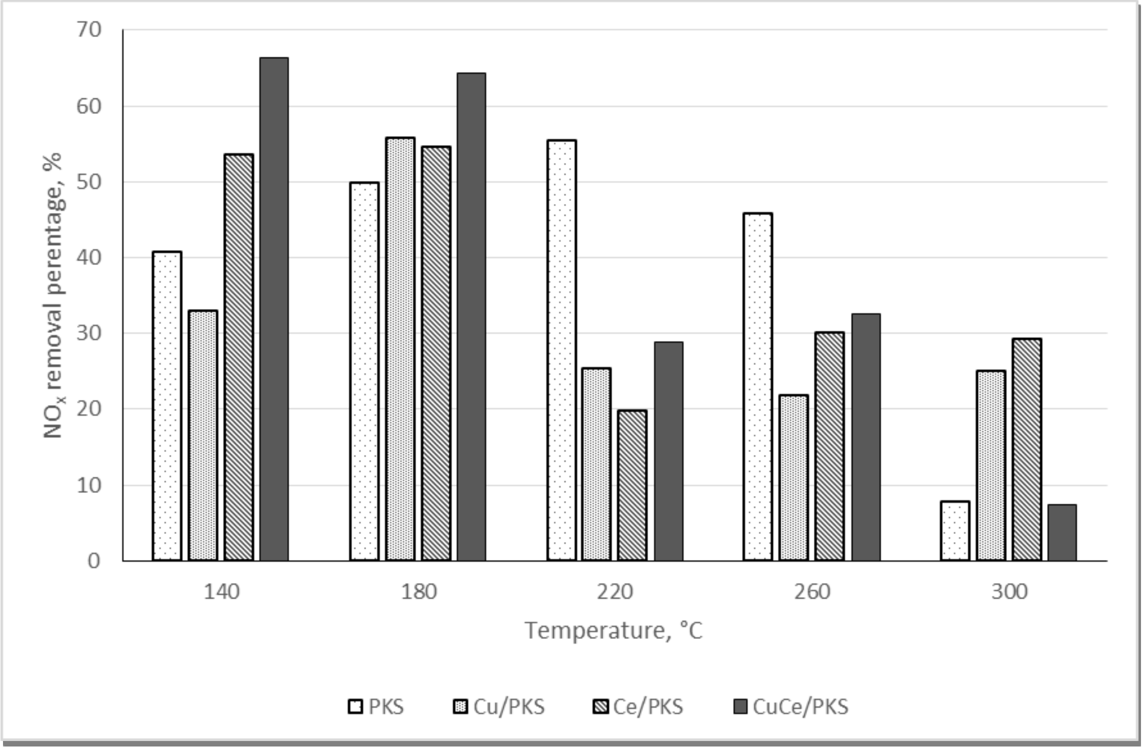

Figure 1. NO_x removal percentage at different temperatures.

This showed that Cu-Ce/PKS exhibited a synergistic effect at low temperature. The increase in catalytic activity because of the interactions between Cu and Ce was also reported by other studies [15] [16]. The composition and distribution of transitional metal catalysts in all samples are obtained using XRF, which is presented in Table 1. It shows that Cu-Ce/PKS had an improved metal distribution in comparison to the monometallic catalysts. Ce/PKS had a poor metal distribution on the carbon surface that could be due to its aggregation affinity, but the loading was better than Cu/PKS. However, the interaction between Cu and Ce in Cu-Ce/PKS caused higher loading of Cu and less aggregation by Ce, which resulted in a homogeneous catalysts distribution. Pang et al. (2014) [15] suggested that Ce was responsible for improving the metallic catalyst distribution and for reducing the aggregation of bimetallic Cu-Ce when impregnated on ZMS-5.

Table 1. Metals composition and distribution from XRF analysis.

Catalyst	Weight of metal oxide (%)						Standard deviation
	CuO	CeO_2	SiO_2	K_2O	CaO	SO_3	
Cu/PKS	82.6	0	14.58	1.14	0.74	0.94	0.065
Ce/PKS	0	91.2	6.83	0.62	0.37	0.89	0.150
Cu-Ce/PKS	64.95	14.57	17.33	1.17	0.97	1.02	0.058[a] 0.057[b]

*a denotes standard deviation of copper; b denotes standard deviation of cerium

On the contrary, very low NO_x reduction was obtained when Cu-Ce/PKS was applied at higher temperature, which is similar to PKS. This suggests that the performance of the bimetallic catalyst depends highly on the carbon support, where the reduced ability of the support to adsorb NO_x at high temperature affects the reduction process by the catalysts. This is discussed further in the following section.

3.2. Role of the palm kernel shell activated carbon as a catalyst support

The passive catalytic removal of NO_x was also performed using raw PKS to study the role of the catalyst support. It was observed (from Figure 1) that the reduction increased with increasing temperature up to 220 °C. Beyond this temperature, PKS showed reduced in performance, where it severely dropped at the highest temperature by almost 40 %. Some research groups suggested that the decrease in the performance of carbon-based catalyst at high temperature was due to the reduced amount of NO_2 being adsorbed by the carbon support [17] [18].

The NO_x adsorption was known to be correlated with the BET surface area [19] [20] [21]. Table 2 shows that PKS had the largest surface area and pore volume followed by Cu/PKS and Cu-Ce/PKS that had similar value, and the least was Ce/PKS. From Figure 1, the NO_x removal performance at PKS's optimal temperature (220 °C) showed this identical trend which validated the fact that BET surface area was an important property to a good SCR catalyst. However, at other temperatures, this was not the case, and the catalytic activity of a catalyst depended on other factors such as surface functional groups [22] [23] [24].

Table 2. Surface area and pore volume for PKS and its derivative catalysts.

Sample	BET Surface area (m^2/g)	Pore volume (cm^3/g)
PKS	1126	0.5260
Cu/PKS	762	0.3716
Ce/PKS	563	0.2550
Cu-Ce/PKS	707	0.3281

Figure 2 compares the FTIR peaks of all samples which resemble the change in the surface functional groups upon different metals impregnation. It can be seen between peaks 3600 and 4000 cm^{-1} that PKS contained unsaturated surface functional group (C=C-H) which was the characteristic band of activated carbon. This group was diminished after the synthesis of the catalyst as the peaks were not observable in all of the catalyst samples showing the utilization of this bond as catalytic anchoring sites. In addition, other oxygenated groups (1600-1800 cm^{-1}) that can be found in PKS were shifted in the catalyst samples showing the used-up of these sites as the metallic catalyst bonding to the surface [25].

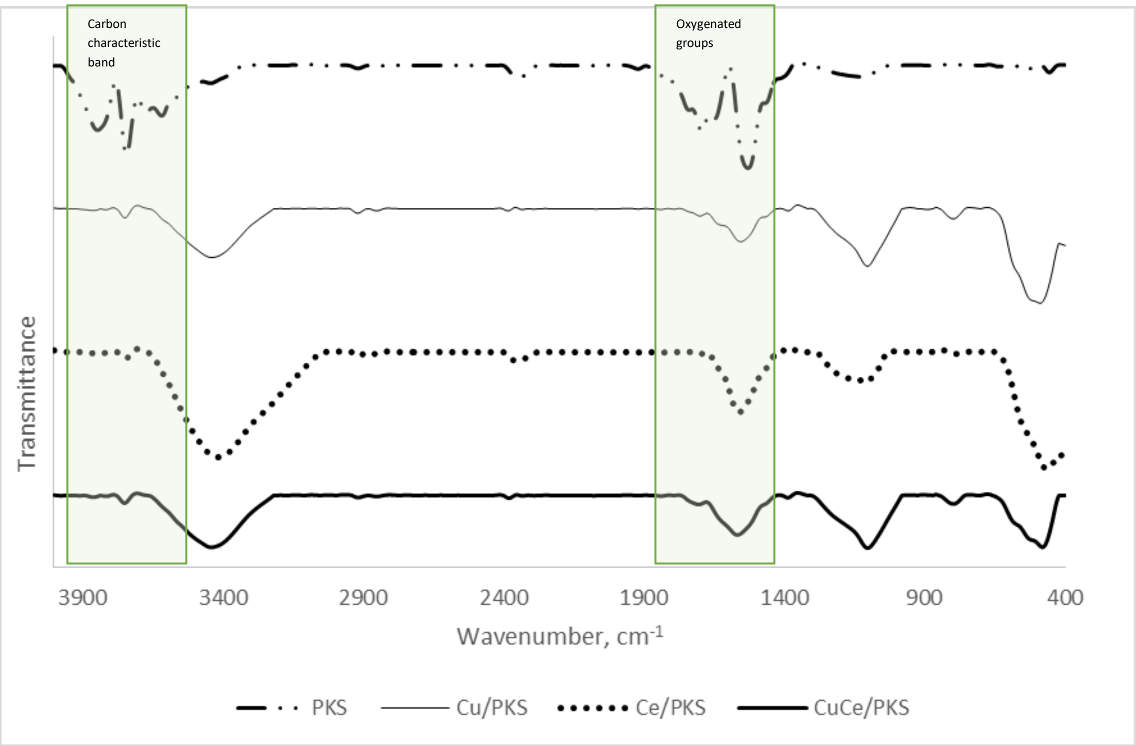

Figure 2. FTIR spectra for PKS, Cu/PKS, Ce/PKS and Cu-Ce/PKS.

3.3. Effects of copper

As copper was deposited on PKS, the removal efficiencies dropped at most of the temperatures, especially above 180 °C (refer figure 1). Chen et al. (2015) [19] used an ordered mesoporous carbon as catalyst support and found that the overall catalytic activity increased with increasing temperature of up to 250 °C before severely dropped when copper was embedded in a cerium-based catalyst. In a separate study and under hydrocarbon environment, Iwamoto et al. (1991) [26] explained that copper is not deactivated, but the oxidation of hydrocarbon at high temperature caused the decrease in the NO_x conversion.

However, the optimum removal temperature was shifted to the lower range that was from 220 °C for PKS to 180 °C for Cu/PKS. Most of the optimum temperatures for copper-supported catalysts reported in the literature were above 200 °C, but Zhu et al. (2015) [27] found that Fe-Cu/ZSM-5 catalyst possessed optimum temperature starting at 180 °C. The lowered optimum temperature is especially favoured in the application of vehicles and industrial de-NO_x system for the lower cost and energy recovery potentials [28].

The catalytic activity of copper at low temperature can be attributed to its reducibility property at such condition. The reduction of CuO may occur in one to two steps. The two-step common sequential reduction for CuO and Cu_2O is represented by equations (1) and (2) whereas equation (3) shows the direct reduction pathway of CuO [29].

$$2CuO + H_2 \rightarrow Cu_2O + H_2O \tag{1}$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \tag{2}$$

$$CuO + H_2 \rightarrow Cu + H_2O \tag{3}$$

Generally, H_2-consumption profile for Cu catalyst is represented by three peaks at around 230, 430 and 550 °C. The first and the third peaks could be assigned to the reduction of isolated Cu^{2+} to Cu^{+} and furthered to Cu^{0}, respectively. The other peak was due to the direct reduction of CuO to Cu^{0} [30]. However, Figure 3(b) shows only one peak appeared at 311 °C for Cu/PKS on top of the peaks occurring for PKS in Figure 3(a). The broad peak at the highest temperature was contributed by the hydrogenation by carbonaceous species [30]. Therefore, it can be inferred that the partial reduction of Cu^{2+} species contributed to the Cu/PKS catalytic activity. Similar reduction activity can be seen for Cu-Ce/PKS in Figure 3(d).

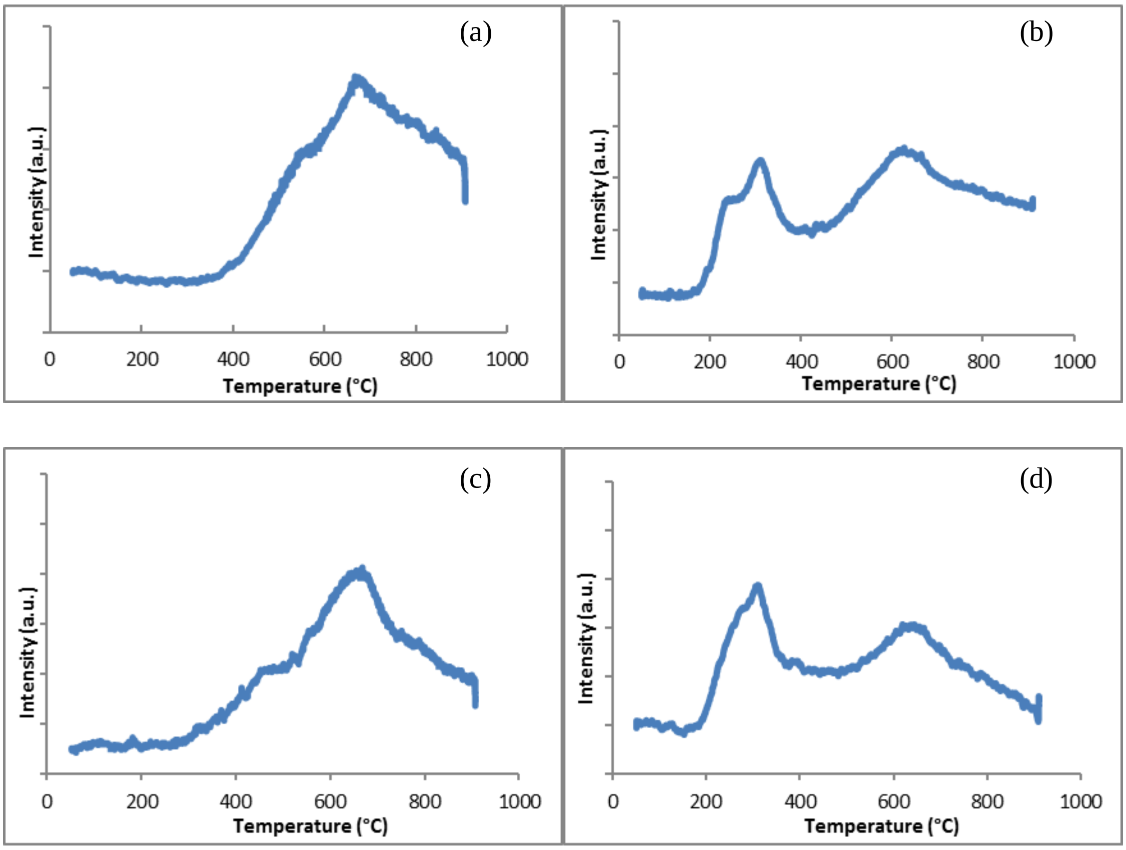

Figure 3. TPR profiles of (a) PKS; (b) Cu/PKS; (c) Ce/PKS; and (d) Cu-Ce/PKS.

3.4. Effects of cerium

Figure 1 shows that at the temperature equal to the PKS's optimum NO_x removal temperature, Ce/PKS's capacity for NO_x removal dropped drastically by 35 %. This was due to the lower surface area and pore volume of the catalyst, as discussed in the previous section (see Table 2). In addition, it was suggested that the deactivation of Ce/PKS occurred at high temperature due to the sintering of the metal particles that leads to a loss of metal surface area and to the loss of CeO_2 surface area. As a result, cerium may have lower oxygen storage capacity (OSC) at this temperature [31].

However, the de-NO_x performance and temperature window for Ce/PKS were higher than PKS at low temperature. This showed that Ce had widened the temperature window for SCR at low temperatures. Other cerium-based bimetallic catalysts were also found to possess a low-temperature window below 180 °C [16] [32] [33]. However, Lamacz et al. (2013) [34] reported a higher temperature window (215-325 °C) for $CuO/CeZrO_2$ catalyst in HC-SCR.

Figure 3(c) shows that Ce/PKS had lower hydrogen reduction activity as compared to PKS. As pure CeO_2 was reported to have reduction peaks at 523 and 658 °C, this implied that Ce was deposited deep inside the heteroatoms of the carbon that had a wide reduction peak from 400 to 900 °C [35]. Besides, the increased performance in comparison to PKS suggested that Ce had assisted in releasing and storing oxygen, as discussed by Chu et al. (2015) [36]. This is an important step in an SCR as chemisorbed oxygen is used to convert NO to NO_2 in the fast SCR mechanism [37].

4. Conclusion

A passive nitrogen oxides removal system consisting of carbon-supported transitional metal catalyst without the use of ammonia was studied. A bimetallic copper-cerium catalyst was impregnated onto palm kernel shell activated carbon as catalyst support via a deposition-precipitation method. The catalyst was tested in a passive catalytic removal of an in-situ NO_x generation by a diesel engine. The highest total NO_x removal was 66 % at 140 °C by Cu-Ce/PKS. An XRF analysis showed that the Cu-Ce synergistic effect improved the metal distribution on the carbon surface. PKS plays an important role in providing the high surface area and, the unsaturated and oxygenated surface functional groups for the adsorption of NO_x species. As copper is reducible at low temperature, it is reactive and is seen to lower the optimum temperature of the catalyst. Cerium, on the other hand, widening the temperature window for the reaction. In conclusion, this biomass-carbon catalyst has a high potential to be developed into an efficient NO_x removal catalyst. Therefore, it is pertinent to continue focusing on the development of the bimetallic catalysts deposited on PKS for low-temperature passive SCR application.

Acknowledgements

The authors acknowledge Universiti Malaysia Sarawak for the Cross-Disciplinary Research grant F02/CDRG/1843/2019 as well as Catalysis Science and Technology Research Centre (Universiti Putra Malaysia) and Nanotechnology & Catalysis Research Centre (Universiti Malaya) for the research facilities.

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