

HC-SCR: NO_x Reduction using Mn and Cu Catalysts Impregnated in Coconut and Palm Kernel Shell Activated Carbon

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Abstract. The characteristics of catalysts impregnated in coconut shell (CS) and palm kernel shell (PKS) activated carbon were determined as potential precursors of catalysts used in a flue gas denitrification system at low temperature. In this study, Manganese (Mn) and Copper (Cu) with metal loading of 8% were impregnated in the activated carbon (AC) before undergoing low temperature calcination process. The morphological properties of samples was analysed using Scanning Electron Microscopy (SEM) and Brunauer, Emmett and Teller (BET) was used to determine the surface area and pore size of samples. The exhaust gas from a diesel engine at a constant flow rate of 4L/min was passed through in a fixed-bed catalytic reactor containing the catalyst, and the concentration of NO_x was measured for temperatures ranging from 150°C to 250°C. It was found that the CS catalysts (CS-Mn and CS-Cu) and PKS catalysts (PKS-Mn and PKS-Cu) have the potential to reduce NO_x concentration, and results showed that the metal loading of 8% resulted NO_x reduction ranging from ~48% to 64%.

1 Introduction

Nitrogen oxides (NO_x) are among the severe contaminants released by automobiles and other vehicles, and by manufacturing industries. Diesel-powered vehicles are becoming more sought after due to their excellent fuel efficiency and less emission of CO₂ compared to their stoichiometric spark triggered gasoline counterpart [1]. Three ways catalysts (TWCs), one of the strategies for NO_x conversion, is reported to produce excess of oxygen contributing to the incapability of catalyst in reducing NO_x from lean burn engine exhaust [2]. Hence, a major challenge today is to minimize NO_x emissions from lean-burn diesel engine exhausts.

Selective Catalytic Reduction (SCR) has been experimented and applied as one of the efficient ways to reduce NO_x emission into the environment [3]. The most extensively used in the industries are NH₃-SCR, which uses ammonia gas as reductant, and HC-SCR that is using hydrocarbon as the alternative for reducing agent. In this case, HC-SCR is the most promising method to control the emission of NO_x from diesel engine vehicles due to the simplicity of system as it does not require an extra gas tank installed because hydrocarbon (HC) itself can act as reducing agent and onboard fuel as reductant [4]. This means, the system, which operated under lean conditions, exploits the unburned hydrocarbon that are already present in the gas stream of the diesel engine exhaust [5].

Catalytic reduction systems usually use precious metal-based catalysts, for instance, Rhodium(Rh), Platinum(Pt), and Palladium(Pd) supported-oxide. Owing to their abilities that is water vapor resistant and SO_x poisoning, these metals are capable of performing efficient NO_x abatement in low operation temperature (lower than 300°C). A study claimed that Pt based catalysts, however, exhibit two downsides namely low N₂ selectivity and narrow temperature window system for reduction of NO_x [6]. On the other hand, Rh based catalysts are mostly used in three ways catalysts (TWCs) operation as Rh metal promotes the best NO_x reduction under low activity temperature; however, it is also said that the catalysis activity involved in synthesis gas conversion process [7].

Other metals that have also been studied for SCR catalysis process are such as Manganese (Mn), Titanium (Ti), Nickel (Ni) and Copper (Cu). These metals are believed to have the capability to remove NO_x gas under low operation temperature especially from stationary sources [8]. However, the potential of these metals have yet to be broadly looked into hydrocarbon SCR systems as they are mostly investigated in urea-SCR. In this study, Mn and Cu are selected as metallic catalysts for the removal of NO_x under low catalytic activity temperature owing to their chemical properties such as alkali metal resistance of catalysts for diesel exhaust treatment [9].

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The mechanism of HC-SCR is complex. As concluded by Lamacz et al. (2013) in a proposed model, when hydrocarbons are unable to undergo oxidation process to CO₂ and H₂O at the dissociation temperature of NO, which contributing to the formation of N₂, it is obligatory to make use of three-function catalysts. Oxidation of NO to NO₂ is the first function of this catalyst. The second function denoted by the hydrocarbons undergoing mild oxidation by NO₂ to oxygenate species which is presumed to be vital for regeneration process of catalyst. In the third function, N₂ is being released in the dissociation of NO_x (via a dinitrosyl-adsorbed intermediate) prior to the N₂ formation and generation of adsorbed oxygen species. The overall activated reductant (C_xH_yO_z) oxidation process resulting in the removal of adsorbed oxygen species. As stated by this research group, function 2 and 3 are said to happen simultaneously, however, both of these functions are not in the same cycle of catalysis at molecular level [10].

A novel establishment of an alternatively sourced carbon-supported catalysts, for instance, activated carbon, bio-char and virgin biomass waste residue, has been developed which is believed to contribute to a more environmental friendly and cost effectiveness [11] for managing the emission of NO in SCR de-NO_x process under low operation temperature [12]. In this study, a laboratory scale reactor was carried out for the purpose of determining the efficiency of NO_x reduction under HC-SCR low temperature using activated carbon derived from coconut and palm kernel shell as catalysts support for Mn and Cu metals. The relation of the physical properties of the catalysts support with the reduction of NO_x was also analysed.

2 Materials and Method

2.1 Preparation of catalyst

Prior to the impregnation process the coconut shell activated carbon (CSAC) and the palm kernel shell activated carbon (PKSAC) was sieved to give uniform particle size of 1 mm. Both CSAC and PKSAC were impregnated with metal nitrate of an appropriate concentration to obtain 8% of metal content per gram of activated carbon. In this study, manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O) from ACROS ORGANIC, and copper (II) nitrate-trihydrate (Cu(NO₃)₂·3H₂O) from SYSTERM ChemAR were used as the metal precursors.

During the impregnation, the solution of metal nitrate was continuously mixed with activated carbon for 5 hours. Then, the samples were heated to 70 °C while being constantly stirred until all the liquid evaporated. After that, the samples were dried in an oven at 110 °C for a period of 12 hours. Finally, the prepared samples were heat-treated at 300 °C for 4 hours. The catalysts that impregnated with 8% (w/v) of metallic catalysts denoted as CS-Mn8, CS-Cu8 and PKS-Mn8, PKS-Cu8.

2.2 Catalyst performance test

Experiments were carried out in a fixed-bed reactor that was filled with the catalyst. The schematic diagram of the experimental setup is shown in Figure 1. The prepared catalysts of CS and PKS were each weighed 10 g and placed on borosilicate glass wool (0.5 g) in the center of the sample holder. The sample holder containing the catalyst was placed inside the fixed-bed reactor after the set temperature was reached. Temperature used here was between 150 – 200 °C.

A stream gas from diesel engine was passed through the prepared catalyst, which act as sorbent and also as SCR catalyst. The feed flow through the sample holder was controlled at 4L/min. The concentration of NO_x in the inlet and outlet of the reactor was measured using Flue Gas Analyzer for a duration of 5 minutes. The reduction efficiency was calculated using the relationship denoted by the following equation:

$$\% \text{ of NO}_x \text{ reduction} = \frac{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{x,\text{in}}} \times 100\% \quad (1)$$

NO_{x,in} denotes the inlet NO_x concentration (vol %) in the stream gas introduced into the fixed-bed reactor and NO_{x,out} denotes the outlet NO_x concentration (vol %) in the stream gas out of the reactor.

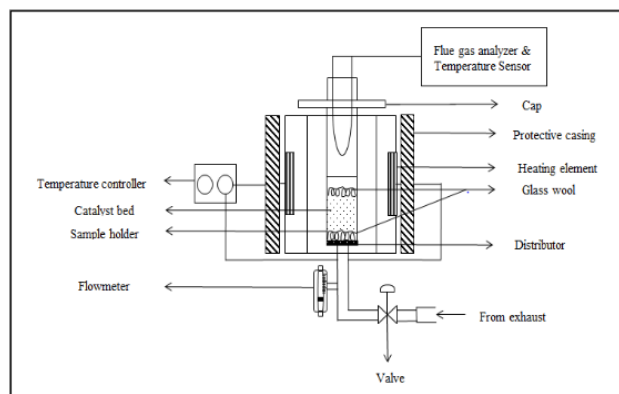


Figure 1 The schematic diagram of the experimental apparatus.

2.3 Catalysts characterizations

The properties of the activated carbon that was impregnated with 8% of Mn and 8% of Cu were analysed based on their surface area, pore size and the images showing the morphological properties that obtained from the experimental work done using Brunauer, Emmett and Teller (BET) and Scanning Electron Microscopy (SEM) apparatus. The metallic catalysts derived from palm kernel shells and coconut shells activated carbon denoted as PKS-Mn8, PKS-Cu8, CS-Mn8 and CS-Cu8.

3 Results and Discussions

3.1 BET analysis

Table 1 Physical properties of raw CSAC, PKSAC and CS- and PKS- based catalysts.

Sample	SA BET (m ² /g)	Pore volume (cm ³ /g)
Raw CSAC	1244	0.416
CS-Mn8	997	0.365
CS-Cu8	1003	0.373
Raw PKSAC	1231	0.399
PKS-Mn8	976	0.338
PKS-Cu8	992	0.350

Physical properties of CS and PKS-based catalysts were investigated in BET analysis as shown in **Table 1**. From the analysis, it can be seen that the specific surface areas and the volume of micropore of both types of activated carbon samples decreased after the process of impregnation of metal. It is presumed that the partial pores were blocked by the particles of metals. This has been proven by several studies saying that metal embedded onto the support filled the micropores but will not affect the performance of the reduction activities [13 - 15]. Impregnation method has proved that the metal particles are successfully located in the pores especially in the internal part, hence, plugging the tapered microporosity. As a result, this fact contributes to the first proof of dispersion of metal on the surface of both activated carbons in high degree.

The difference in the surface area and pores in BET analysis was supremely low among the impregnated of both CSAC and PKSAC stipulating the percentage of metal loadings impregnated onto the surface of activated carbons were almost equal.

3.2 SEM analysis

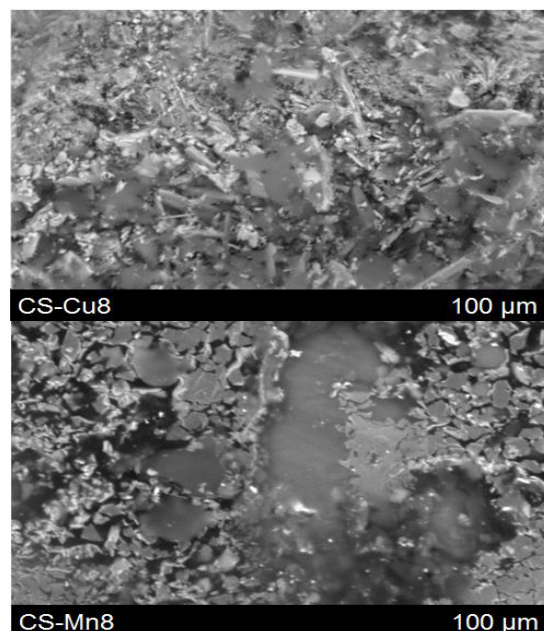
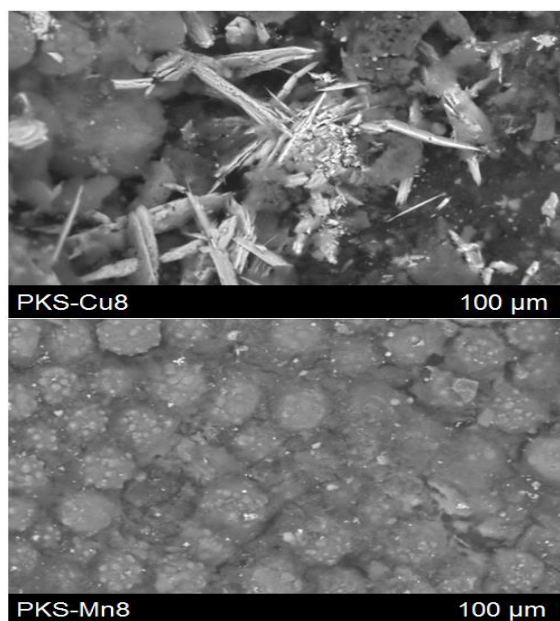


Figure 2 SEM result for PKS-Cu8, PKS-Mn8, CS-Cu8 and CS-Mn8.

The catalysts' surfaces and morphologies which undergone the process of impregnation of metals are shown in **Figure 2**. Comparing between the two types of activated carbon support, smoother and better consistency dispersion of metal was observed for the coconut shells activated carbon support than those obtained for palm kernel shells activated carbon. This can be deduced that the nature of the CSAC reacted well with both Mn and Cu metals. Consequently, better dispersion of metals can be observed over the surface found for CSAC, which is also predicted to promote better catalytic efficiency. Tang et al. (2015) had proved that the impregnation method to prepare catalyst provided a better dispersion and formation of metal solution which will encourage the catalytic activity [13].

3.3 NO_x reduction

In **Figure 3**, comparing between the performance of raw CSAC and PKSAC, it is shown that CSAC adsorbed NO_x better than PKSAC with percentage adsorption of NO_x estimated to be 28% and 22%, respectively. However, in this case, only adsorption process can be observed because there is no reaction between metal catalysts with hydrocarbon (HC). This is because the obvious difference in the surface area and size of pores of the AC to facilitate the adsorption of NO_x molecules in **Table 1**. In addition to that, owing to favorable surface area and pores size, the performance of metal catalysts impregnated on CSAC shows better efficiency if compared to that in PKSAC. This trend is aligned with findings by Guera et al. (2016) where limited surface area and low porosity of activated carbon small amount of adsorbed N₂ [14].

According to SCR mechanisms by M. Adamowska-Tessier (2015), there are 3 functions of SCR mechanisms, which is respectively the oxidation of NO to NO₂ in the

first function, followed by mild oxidation of hydrocarbon (HC) in the second and, finally, the conversion of NO_2 to N_2 happens in the third function. **Figures 4 (a) and (b)**, show the percentage of NO_x reduction versus time. The reading recorded at zero minute is the reading taken for the NO_x concentration before the exhaust gas entered the reactor that was filled with catalyst, which gives zero NO_x reduction. The concentration of NO_x in the exhaust gas that came out from the reactor was measured for 5 minutes, and the % of NO_x reduction was found to be higher for the activated carbon impregnated with Cu compared to that impregnated with Mn. The addition of metal onto the activated carbon resulted in the increase in the % of NO_x reduction as illustrated by results shown in Figures 3 and 4; The % of NO_x reduction for raw CS was found to be about 28%, as shown in Figure 3 while that for CS with Cu and Mn was increased to above than 50%. Here, the increase in the % of NO_x reduction indicates the effect of SCR reaction, which can be observed in the first 30 seconds as the actual conversion of NO_x into N_2 , as in the third function of the mechanisms, happened during that time frame. The % of NO_x reduction was found to decrease gradually, which may be due to the trapped NO_x that filled the pores of the activated carbon.

Based on studies conducted by Surjit Singh et al. (2013), he found that the optimum reduction of NO_x was only 25% under temperature of 200 °C. The flow rate of the flue gas used in his study was at 1L/min, which may contribute to the low NO_x reduction. However, the percentage of NO_x reduction in the study increased to 67% as the temperature was elevated to 280 °C, which may indicate higher NO_x conversion [12]. The % of NO_x reduction for different samples of catalyst analysed in this work was compared as shown in **Figure 5**.

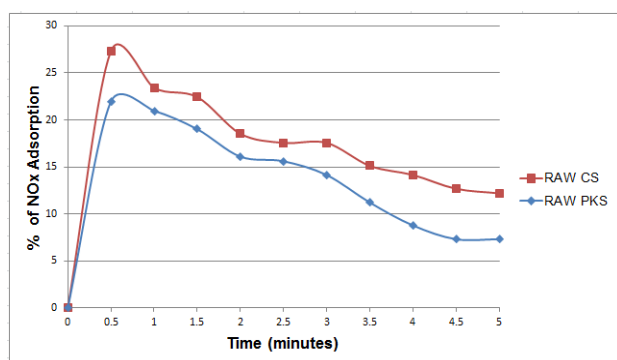


Figure 3 NO_x adsorption percentage as the function of time for raw CSAC and PKSAC at temperature of 200 °C and flow rate of 4L/min.

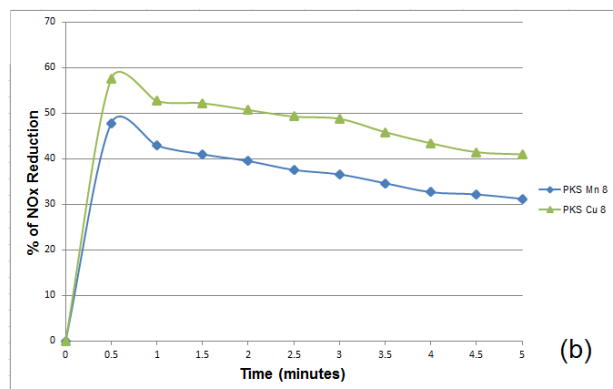
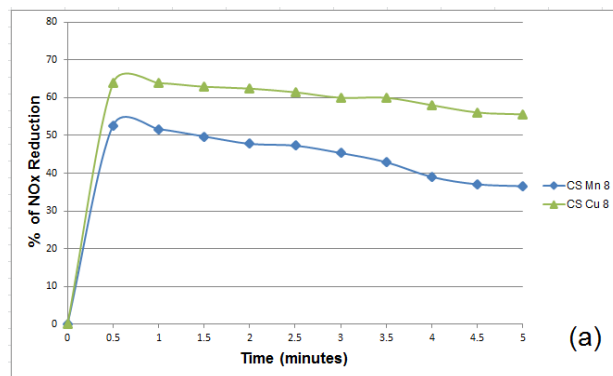


Figure 4 The % of NO_x reduction as a function of time for (a) CS-Mn8 and CS-Cu8, (b) PKS-Mn8 and PKS-Cu8 under temperature of 200 °C, flow rate of 4L/min.

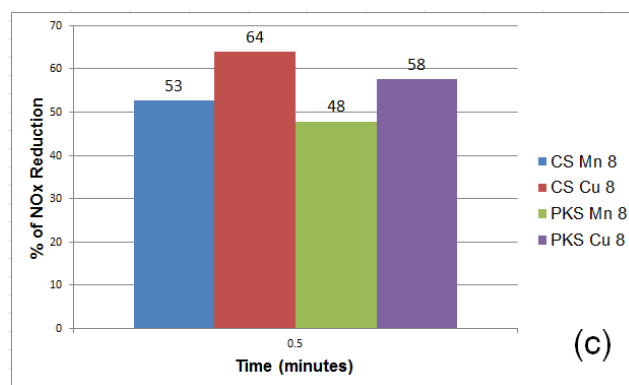


Figure 5 The overall result of NO_x reduction as a function of time for CS-Mn8 (53%), CS-Cu8 (64%), PKS-Mn8 (48%) and PKS-Cu8 (58%) under temperature of 200 °C, flow rate of 4L/min.

3.4 Effect of metal type

Figure 4 (a) and (b) showed the results of NO_x reduction using the catalyst impregnated onto the activated carbon derived from coconut shells, as shown in Figure 4 (a) and from the palm kernel shells, as shown in Figure 4 (b) with 8% of Mn and Cu. Comparing between the potential of metal Cu and Mn in catalytic activities, it was found that both curves in (a) and (b) showed Cu gives better reduction of NO_x . The % of NO_x reduction

was estimated to be 64% and 58% for CS-Cu8 and PKS-Cu8, respectively.

Results obtained here may suggest that Cu that has higher electronegativity has a greater tendency to attract electron toward its atom resulting in higher NO_x reduction. Consequently, owing to this nature, Cu makes a better catalytic metal than Mn.

4 Conclusions

This study emphasized on the effect of manganese and copper impregnated onto biomass waste derived activated carbon combined as Selective Catalytic Reduction (SCR) by using hydrocarbon (HC) as the reduce agent. Based from the observations and results obtained, it can be concluded that coconut shells activated carbon based metal catalysts was found to give better reduction of NO_x compared to palm kernel shells activated carbon based catalysts.

CSAC based catalysts shows a catalytic effect towards the removal of NO_x as well as active, selective towards NO_x and was observed stable in laboratory testing condition. From the results, Cu is a better catalyst for the SCR reaction than Mn as it has been proven that the combination of Cu and coconut shell activated carbon showed better NO_x removal.

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References

- [1] C. Zhu, S. Liu, H. Liu, J. Yang, X. Liu, and G. Xu, "NO_x emission characteristics of fluidized bed combustion in atmospheres rich in oxygen and water vapor for high-nitrogen fuel," *Fuel*, vol. 139, pp. 346–355, 2015.
- [2] P. M. More, N. Jagtap, A. B. Kulal, M. K. Dongare, and S. B. Umbarkar, "Applied Catalysis B : Environmental Magnesia doped Ag / Al₂O₃ – Sulfur tolerant catalyst for low temperature HC-SCR of NO_x," *Applied Catal. B, Environ.*, vol. 144, pp. 408–415, 2014.
- [3] B. Sawatmongkhon, a. Tsolakis, S. Sitshebo, J. Rodríguez-Fernández, M. Ahmadinejad, J. Collier, and R. R. Rajaram, "Understanding the Ag/Al₂O₃ hydrocarbon-SCR catalyst deactivation through TG/DT analyses of different configurations," *Appl. Catal. B Environ.*, vol. 97, no. 3–4, pp. 373–380, 2010.
- [4] H. Gu, K. M. Chun, and S. Song, "The effects of hydrogen on the efficiency of NO_x reduction via hydrocarbon-selective catalytic reduction (HC-SCR) at low temperature using various reductants," *Int. J. Hydrogen Energy*, vol. 40, no. x, pp. 1–9, 2015.
- [5] Y. J. Kim, H. J. Kwon, I. Heo, I. S. Nam, B. K. Cho, J. W. Choung, M. S. Cha, and G. K. Yeo, "Mn-Fe/ZSM5 as a low-temperature SCR catalyst to remove NO_x from diesel engine exhaust," *Appl. Catal. B Environ.*, vol. 126, pp. 9–21, 2012.
- [6] P. M. More, D. L. Nguyen, P. Granger, C. Dujardin, M. K. Dongare, and S. B. Umbarkar, "Activation by pretreatment of Ag–Au/Al₂O₃ bimetallic catalyst to improve low temperature HC-SCR of NO_x for lean burn engine exhaust," *Appl. Catal. B Environ.*, vol. 174–175, no. x, pp. 145–156, 2015.
- [7] M. Adamowska-Teyssier, A. Krztoń, P. Da Costa, and G. Djéga-Mariadassou, "SCR NO_x mechanistic study with a mixture of hydrocarbons representative of the exhaust gas from coal combustion over Rh/Ce_{0.62}Zr_{0.38}O₂ catalyst," *Fuel*, vol. 150, no. x, pp. 21–28, 2015.
- [8] M. Kang, E. D. Park, J. M. Kim, and J. E. Yie, "Manganese oxide catalysts for NO_x reduction with NH₃ at low temperatures," *Appl. Catal. A Gen.*, vol. 327, no. 2, pp. 261–269, 2007.
- [9] H. Taghavifar, H. Taghavifar, A. Mardani, and A. Mohebbi, "Modeling the impact of in-cylinder combustion parameters of di engines on soot and NO_x emissions at rated EGR levels using ANN approach," *Energy Convers. Manag.*, vol. 87, pp. 1–9, 2014.
- [10] A. Łamacz, A. Krztoń, and G. Djéga-Mariadassou, "Study on the selective catalytic reduction of NO with toluene over CuO/CeZrO₂. A confirmation for the three-function model of HC-SCR using the temperature programmed methods and in situ DRIFTS," *Appl. Catal. B Environ.*, vol. 142–143, no. 2, pp. 268–277, 2013.
- [11] C. K. Seo, H. Kim, B. Choi, M. T. Lim, C. H. Lee, and C. B. Lee, "De-NO_x characteristics of a combined system of LNT and SCR catalysts according to hydrothermal aging and sulfur poisoning," *Catal. Today*, vol. 164, no. 1, pp. 507–514, 2011.
- [12] S. Singh, M. A. Nahil, X. Sun, C. Wu, J. Chen, B. Shen, and P. T. Williams, "Novel application of cotton stalk as a waste derived catalyst in the low temperature SCR-deNO_x process," *Fuel*, vol. 105, pp. 585–594, 2013.
- [13] W. Tang, X. Wu, S. Li, X. Shan, G. Liu, and Y. Chen, "Co-nanocasting synthesis of mesoporous Cu-Mn composite oxides and their promoted catalytic activities for gaseous benzene removal," *Appl. Catal. B Environ.*, vol. 162, pp. 110–121,

2015.

- [14] N. Gutiérrez-Guerra, L. Moreno-López, J. C. Serrano-Ruiz, J. L. Valverde, and A. de Lucas-Consuegra, “Gas phase electrocatalytic conversion of CO₂ to syn-fuels on Cu based catalysts-electrodes,” *Appl. Catal. B Environ.*, vol. 188, pp. 272–282, 2016.
- [15] S. Sumathi, S. Bhatia, K. T. Lee, and a. R. Mohamed, “Selection of best impregnated palm shell activated carbon (PSAC) for simultaneous removal of SO₂ and NO_x,” *J. Hazard. Mater.*, vol. 176, no. 1–3, pp. 1093–1096, 2010.