The potential for using a coconut shell catalyst for the selective catalytic reduction of NOx gases

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Abstract

Selective Catalytic Reduction (SCR) is a promising technique in mitigating the drawbacks of combustion system. This study investigated the potential of using coconut shell activated carbon (CSAC), an abundant and inexpensive resource, as an SCR catalyst support for sustainable energy generation. Local CSAC was physically treated by co-impregnating with Copper (Cu) and Manganese (Mn) oxides. The modified samples were then calcined under low temperature. Properties of all three types of samples were then characterized and analysed using Temperature-Programmed Reduction (TPR), X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR). Results showed that CSAC can be an effective SCR catalyst to obtain higher conversion of NOx gases into non-toxic gas.

Keywords: biomass combustion, NOx gases, SCR, Cu-Mn catalyst, coconut shell activated carbon, carbon support, low-temperature calcination, TPR, XRF, FT-IR.

1 Introduction

Biomass have been converted into energy since thousands of years ago but the development of the technology for sustainable utilization of biomass did not start until 1812 when a gas company in England demonstrated the pyrolysis of biomass

into liquid fuel [1]. The initiative was adopted to reduce the world dependency on fossil fuels. In fact, by utilizing biomass from the residues resulted from the harvesting of agricultural crops can eliminate the "food versus fuel" dilemma, reduce land filling activity and complete the lifecycle of carbon dioxide. Nowadays, the path for the conversion of biomass waste into energy is multitudinous which includes combustion, gasification, fermentation and pyrolysis.

Despite the fact that utilizing agricultural waste is greener and sustainable, there are not much fully-operated industrial scale energy generation from waste in developing countries where biomass can be abundantly available [2, 3]. Even though the energy recovery is usually only 35% and in some cases 85%, biomass combustion is the commonest route chosen by developers due to its simple process, low capital cost ($0.19/btu/hr compared to $0.35/btu/hr for gasification) and availability of equipment as well as proven technology which renders comfort investment in the market [4]. However, low energy recovery adversely increase the amount of pollutants being released during combustion process especially NOx and SOx gases and volatile organic compound (VOC).

The two most prominent ways for removal of these air pollutants from combustion process are; gas cleaning technology and Selective Catalytic Reduction (SCR), with the latter being the area of interest lately because of the lower capital cost [5–10]. SCR exploits the reaction of NOx with ammonia to produce the environmentally friendly inert gas, nitrogen [5]. Many types of catalyst have been developed, tested, and used such as titanium dioxide-supported vanadium pentoxide, zeolite H-ZSM5 and 13X-APG, MoO_3/TiO_2-V_2O_5 honeycomb monolith and various combination of Pt, Pd, Rh, Au, Ag, Cu, Co, Fe, In and Ga metals with different supports of zeolite, Al_2O_3, SiO_2 and activated carbon [6–13].

However, metallic support can increase the bulk cost of catalyst utilization and requires high temperature, which means increased operating cost. Yang *et al.* [10] had reviewed on the application of various carbon as catalyst support for flue gas treatment and concluded that activated carbon can be potentially cost-effective especially if the precursor resources are abundant. Therefore, the aim of this study is to investigate the potential of using activated carbon derived from agricultural waste, particularly coconut shell, as a support for SCR catalyst by analyzing its properties through Temperature-Programmed Reduction (TPR), X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR).

2 Materials and methods

2.1 Samples preparation

Three samples were used in this study: coconut shell activated carbon (CSAC), uncalcined coconut shell catalyst and calcined coconut shell catalyst. Local coconut shell activated carbon (CSAC) supplied by Robert Scientific Sdn. Bhd. (properties shown in Table 1) were used as the control samples. Some of the CSAC were physically treated by the following procedures; firstly, they were washed

under running tap water before oven-dried for 24 hrs. CSAC samples were then soaked and stirred in the copper and manganese (Cu-Mn) (1:1) aqueous solution for another day. The slurry was then washed using distilled water and dried at 100ºC. These samples were used as uncalcined coconut shell catalyst (UCSC). Some of the UCSC were then calcined at low temperature to observe the development of the surface upon calcination. These samples were used as calcined coconut shell catalyst (CCSC).

Table 1: Properties of CSAC obtained from supplier.

Properties	Values
Iodine number	Min. 1050
Particle size (mm)	0.59–2.38
Moisture content (%)	Max. 5
Ash content (%)	Max. 3
Ball-pen hardness	Min. 98
Apparent density (kg/m^3)	450–520
BET surface area (m^2/g)	1100–1250
pH	Alkaline

2.2 Characterization and analysis of CSAC, UCSC and CCSC properties

In order to evaluate the potential of CSAC as SCR catalyst, CSAC, UCSC and CCSC samples were analysed using three techniques; X-Ray Fluorescence (XRF), Fourier Transform Infrared (FT-IR) and Hydrogen Temperature-Programmed Reduction (H_2-TPR). Determination of chemical and mineral compositions of all samples was done by using Shimadzu EDX-720/800HS Energy Dispersive X-ray Fluorescence Spectrometer (XRF). The changes in the presence of surface functional groups for all samples were investigated using Bruker Optic GmBH 1997-2000 OPUS Version 3.1 Fourier Transform Infrared Spectrometer (FT-IR). Finally, observation on the reduction behaviour of the catalyst prior to and after calcination step for UCSC and CCSC samples was performed using Thermo Scientific TPDRO 1100 Temperature-Programmed Desorption/Reduction/Oxidation Analyzer.

3 Results and discussions

3.1 Stoichiometric composition of inorganic elements

Inorganic content in all samples is measured using XRF and is shown in Table 2. As copper and manganese oxides were impregnated onto CSAC, intrinsic potassium and calcium ions were replaced by these metals via ion exchange

mechanism. After calcination, only small amounts of Cu can be seen vaporized while slight increase in Mn content is attributed to carbon burn-off. Similar observation was found by Pasel *et al.* [14] on the loading of copper on activated carbon at various activation temperatures.

Table 2:   Stoichiometric composition of inorganic elements in CSAC, UCSC and CCSC.

Elements	Weight % (deviation %)		
	CSAC	UCSC	CCSC
K	69.431 (17.5)	1.793 (2.3)	6.803 (3.4)
Ca	18.862 (16.5)	1.193 (1.6)	2.057 (1.7)
Fe	5.336 (7.5)	nd	nd
Si	2.882 (24.9)	nd	nd
S	2.033 (5.1)	0.648 (3.0)	1.346 (2.7)
Cu	1.456 (4.3)	75.296 (8.4)	59.721 (5.6)
Mn	nd	21.07 (4.4)	30.072 (4.0)

nd: not detectable

By using the same analysis technique (XRF), Thakur *et al.* [15] concluded that low deviation of elemental weight percentage is related to uniform catalyst dispersion on the surface. From Table 2, loading of Cu and Mn using impregnation technique gave a fairly uniform distribution while calcination increased the uniformity of metals loading (4–8% versus 4–6%).

3.2 Changes in surface functional groups

Figure 1 illustrates the FT-IR spectra of CSAC, UCSC and CCSC samples. All samples showed adsorption peaks corresponding to stretching vibration of; (1) OH (3435.89, 3436.33 and 3423.85 cm^{-1}), (2) NH = C (2399.90, 2398.33 and 2393.32 cm^{-1}), (3) N = C (1556.90, 1551.60 and 1569.89 cm^{-1}) and (4) C-O (1162.33, 1164.65 and 1161.03 cm^{-1}) [16].

Peak (1) and (4) are oxygenated surface groups, which are also the anchoring sites for metal catalysts [17]. UCSC showed a reduction in these peaks due to the used-up by Cu and Mn. However after calcination, the absorption peaks reverted which shows Cu-Mn ions being vaporized and dispersed more evenly on the other available sites on the CCSC. This is shown by the appearance of adsorption peak corresponding to an in-plane deformation vibration of C-CO at (5) 524.39 cm^{-1} of CCSC sample [16].

3.3 Catalyst potential indication

Primary indication of catalyst potential for SCR reaction with NOx gases can be evaluated from its reduction behavior, which is displayed in Figure 2 for UCSC and CCSC respectively.
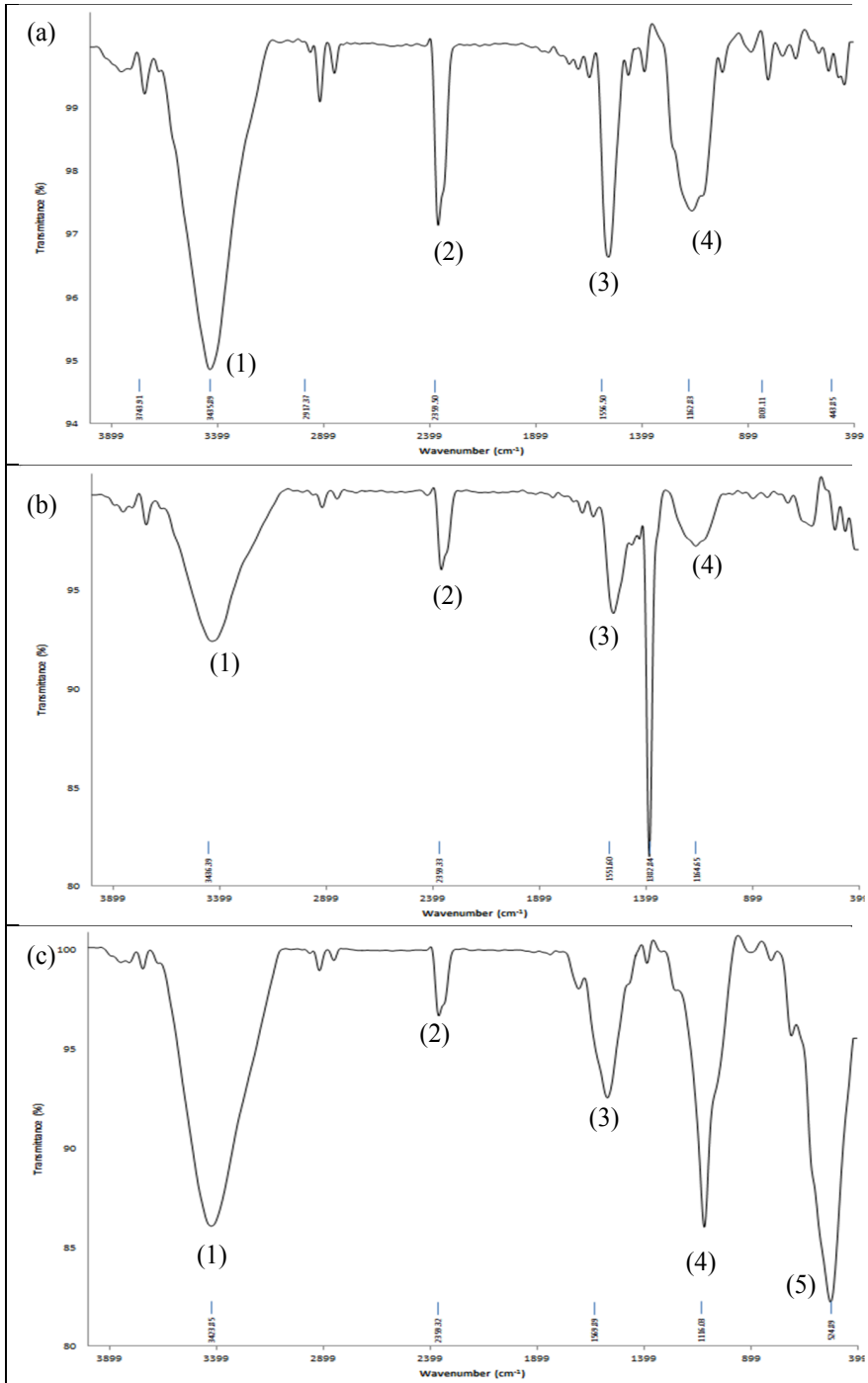
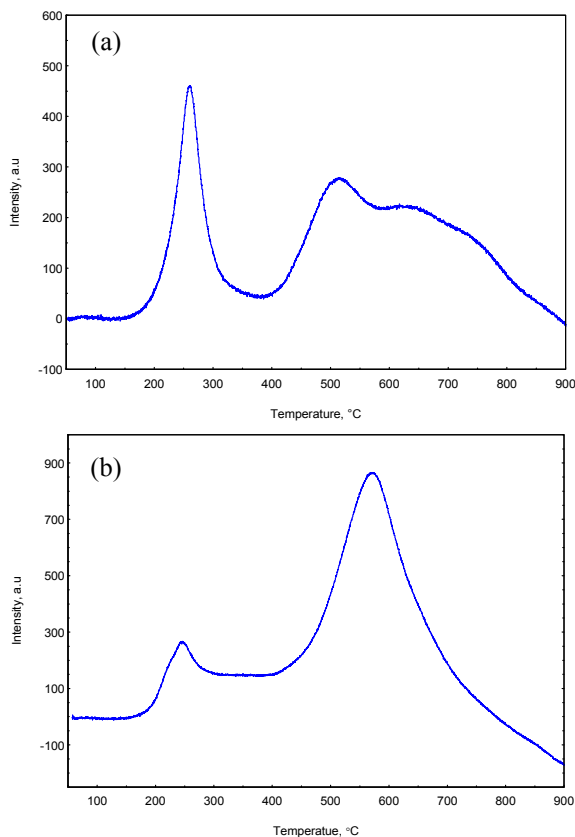Figure 1:   FT-IR spectra of (a) raw CSAC (b) UCSC (c) CCSC.

Figure 2:   Temperature-programmed Reduction (TPR-H$_2$) profile of; (a) UCSC and (b) CCSC.

The peaks at 240–260ºC indicates the reduction of CuO while H$_2$-consumption peaks at 500–600ºC shows the further reduction of CuO and reduction of MnO [17, 18]. It can be observed for CCSC, the intensity of reduction at low temperature decreased and disappearance of shoulder at ~650ºC, which implies that the catalyst has been reduced [19]. It is known that catalyst in its reduced state is reactive in redox reaction [20].

4   Conclusions

Besides possessing considerably high surface area, CSAC contains exchangeable cations and intense oxygenated surface functional groups, hence hypothetically can be considered as a suitable candidate for SCR catalyst support. As Cu-Mn was impregnated on CSAC, it can be seen from XRF results that ions exchange had took place. Furthermore, adsorption at oxygenated surface functional groups shown in FT-IR results, aided the metal loading of the catalyst. Subsequently,

calcination reduced the metals at both low and high temperatures. Based on these results, CSAC has a high potential to be developed as SCR catalyst for reduction of NOx gases. Future investigation is recommended to observe the uniformity and stability of metals loading.

Acknowledgements

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