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Assessment of copper-iron catalyst supported on activated carbon for low-temperature nitric oxide reduction by hydrogen

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Abstract. It is pertinent to assess the performance of a sustainable system that can treat nitrogen oxides (NO_x) emissions from combusting biomass waste. Low-temperature selective catalytic reduction is attractive due to the longer catalyst lifetime and the possibility to use carbon-based catalysts. Hence, this study explores this system with the utilization of: (i) a cost-effective catalyst support, i.e. activated carbon derived from abundant biomass waste; (ii) a renewable reductant, i.e. hydrogen; and (iii) Earth-abundant metal catalysts, i.e. copper and iron. The catalyst was prepared by impregnating metal oxides (Cu and Fe) over palm kernel shell activated carbon (PKS). The catalyst was characterised by hydrogen-temperature programmed reduction (H_2-TPR) and nitric oxide-temperature programmed desorption (NO-TPD). H_2-TPR revealed an increase in the reducibility, attributed to the synergistic effects between Cu and Fe. However, these catalyst sites favour nitrous oxide (N_2O) formation as shown via NO-TPD. Meanwhile, the catalyst activity has also been investigated in a fixed-bed reactor. It showed that the 100% conversion can be achieved at 200°C, but the selectivity towards nitrogen formation is as low as 40%. Therefore, investigating the optimum design of PKSCuFe catalyst is justifiable to improve the performance of low-temperature selective catalytic reduction.

1. Introduction

In developing countries, decomposable organic waste, mainly from agricultural activities, dominates the total solid waste produced (4.5 times more than the generation of municipal solid waste) [1]. Typical final disposal methods are open dumping, landfilling and incineration. The development of methods for the sustainable utilization of solid waste is therefore becoming more prominent [2]. One sustainable alternative in utilizing agro-waste is its conversion to either energy or other useful products, such as composites and activated carbon which have shown successful application in industry. Activated carbon has been utilized widely in wastewater treatment and gas purification processes because it has high adsorption capacity. It is also evident that this material can be potentially utilized in other applications, in particular catalysis. The synthesis and application of carbonaceous catalysts from biomass has recently been reviewed [3]. Additionally, Yang et al. (2011) have reviewed the application of various

carbons as catalyst supports for flue gas treatment and concluded that activated carbon can be a potentially cost-effective catalyst support especially for application at low temperature [4].

The conversion of biomass to energy is associated with the emission of greenhouse gases (GHG) including nitrogen oxides (NO_x) and sulphur oxides (SO_x). Pathways for the conversion of biomass into energy include combustion, gasification, fermentation and pyrolysis [5]. In developing countries, even though the energy recovery is usually only 35 % and in some cases 85 %, incineration/combustion is the most common route chosen by developers due to its simplicity, low capital cost (RM 0.55 M/t compared to RM 0.65 M/t for gasification), low operational cost (RM 102/t compared to RM 120/t for gasification) as well as proven technology [6]. Nevertheless, low energy recovery adversely increases the volume of pollutants being released during combustion processes. These include mercury, NO_x gases and volatile organic compounds (VOCs).

NO_x contributes to air pollution and the release of this substance into the atmosphere is strictly regulated by regulations and protocols of the respective countries. Emission of NO_x promotes acid rain and ground-level ozone (smog). Due to the harm that NO_x has brought upon living things, many techniques have been implemented to control the emission of NO_x concentration including gas cleaning technology and selective catalytic reduction (SCR) with the latter being the area of interest lately because of the low capital cost [4], [7]–[10]. However, the operating cost of SCR can be expensive due to the need for ammonia or urea as the reductant. Therefore, other reducing agents have been studied, with hydrogen emerging as a promising alternative which has the potential to be produced sustainably via electrolysis [11], [12].

Many types of catalyst have been tested for NO reduction with hydrogen (H_2-SCR) including Pt [13]–[16] and Pd [17]–[19]. A study using Pt, Pd and Rh supported over aluminium oxide showed high performance above 200 °C with conversion and nitrogen selectivity of at least 95 % and 80 % respectively [20]. The catalysts were also used with other supports including silica [18], zeolite [21], [22], mixed oxides [23], perovskite [24] and cordierite [25], showing favourable adsorption and reduction of nitric oxide. These catalysts and supports however suffer from sustainability issues around resource scarcity due to high demand. The performance of sustainable catalysts, especially those employing Earth-abundant metals and renewable catalyst supports such as activated carbon should therefore be explored.

Copper salt supported on zeolite has been patented to adsorb NO_x at low concentration and shows competitive performance to the noble metals [26]. Furthermore, it has been shown that copper- and iron-exchanged zeolites are reactive at temperatures below 573 K to reduce NO using hydrocarbons, but their performance is still inferior when compared to noble metals catalysts such as platinum [27], [28].

This work aims to tackle the twin challenges of waste utilization and the development of more active and selective H_2-SCR catalysts. Palm kernel shell (PKS), a major residue in oil palm industry, could be an abundant resource for producing carbon catalyst support due to its high carbon content and large surface area [29]. Therefore, it is used in this work as a sustainable carbon source to synthesize the catalyst support, while Earth-abundant metals (Cu and Fe) are employed as the catalytic active agents, both as single component (Cu or Fe only) and as a binary system (Cu and Fe).

2. Methodology

2.1. Catalyst synthesis
PKS activated carbon was supplied by the Universiti Malaysia Sarawak (UNIMAS). The particles were crushed in a ball mill and sieved to obtain uniform size prior to drying in an oven for 72 h at 110 °C. The catalysts were prepared via incipient wetness where the carbon was dipped in a metal salt solution [30] (either copper nitrate trihydrate, iron nitrate nanohydrate or a mixture of copper and iron nitrate, both at 99.999 % trace metals obtained from Sigma-Aldrich, UK). Co-doping was performed by mixing the metal nitrates on a 1:1 mass ratio, keeping the total metal loading as 10 wt.%. Subsequently, the catalysts were dried at 110 °C overnight, washed with deionized water and dried again at 80 °C for 24 h. All catalysts were calcined in an inert nitrogen flow at 200 °C for 2 h.