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Sustainable and/or waste sources for catalysts: Porous carbon development and gasification

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ABSTRACT

Catalytic processes can be made even more efficient and sustainable if catalysts are obtained from renewable materials and/or materials that are otherwise viewed as waste. Because the interactions between species are complex, however, unexpected results may be obtained when using impure feedstocks. This paper provides a brief overview of the work that has been done to use wastes to prepare catalysts, followed by a more detailed review of our work with petroleum coke, biomass, and biosolids for porous carbon development and gasification. In particular, the challenges of using these materials are discussed. For example, petroleum coke is a much denser source of carbon than biomass but it also contains more contaminants. Although biomass is generally cleaner, it contains a significant quantity of volatile species so that yields are lower. Biomass is a renewable source of catalysts that can be used through co-feeding to enhance the gasification of other feeds. Spent catalysts can also be a good source of gasification catalysts. Regardless of the source, the catalytic species (e.g., nickel or potassium) can be deactivated by other species present, including vanadium on the spent catalysts or silicon and aluminum that are present in the co-feed.

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1. Introduction

Sustainability is important environmentally and economically [1] and so there has been a surge in research devoted to making processes more sustainable or green. Advances in materials have made it possible to completely redesign not only chemical processes but also the way that we do tasks with the goal of leaving a smaller environmental footprint. Catalysts with their ability to make reactions highly selective at less severe conditions are an important component of sustainability. Recently there has been much interest in extending this idea to the development of the catalysts themselves, by sourcing feeds and reactants from waste materials or renewable sources [2]. In addition, the repurposing of spent catalysts for other reactions has been investigated [3].

Two thorough review articles “Waste materials – catalytic opportunities: an overview of the application of large-scale waste materials as resources for catalytic applications” [4] and “Catalytic applications of waste derived materials” [5] summarize the research utilizing waste materials for catalysts. The first review by Balakrishnan et al. outlines the utilization of waste material from large-scale (millions of tons per year globally) industrial and bio-

logical sources, while the second review by Bennett et al. covers a broader range of sources, and illustrates how the topic of valorization of waste for catalysis has rapidly expanded in just five years. The waste materials included red mud, aluminum dross, fly ash, slag from iron manufacture, sludges from various sources, chicken eggshells, shrimp shells, crab shells, snail shells, coconut shells, rice husk, rice husk ash, waste cement, sponge skeletons, seed cakes, starch, goldmine waste, circuit boards, and glycerol. The elements of interest in these waste materials include (note the oxides of the elements may be present and/or of interest) iron, copper, aluminum, silicon, potassium, calcium, carbon, and chromium, while the applications include a wide range of reactions from cracking to hydrogenation to transesterification, and as different catalyst supports including zeolites and activated carbon. There is also interest in using the prepared catalysts, in particular from slag that is rich in CaO, to fixate CO₂ [6].

Of course there are challenges with using these waste materials. The composition of these materials is variable and dependent on both the feedstock and operating conditions of the process from which they were produced [4,6]. The associated impurities in the waste can be problematic, and often the physical properties, such as surface area, of the materials need to be improved [7], but in some cases only calcination is required [5,8]. In supported metal catalysts, increased surface area and porosity are critical for the dispersion of the active phase. For example, nanoscale particles are more resis-

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tant to sintering and deactivation by coking [1]. Clay materials, which are non-toxic, inorganic (mainly aluminosilicate) layered compounds with Brønsted and Lewis acidities, and ion exchange capabilities, have been used in their natural form for some organic reactions [9] but often undergo processing to exchange the ions within the structure, add guest species, or impregnate catalytically active species.

As pointed out in many publications, the conversion of large-scale waste products into catalysts only consumes a small fraction of the waste. Nevertheless, the process that requires the catalyst can be more economical and have less environmental impact when waste is used. Ultimately the trade-off is economic with performance versus cost. For example, if a waste-derived catalyst is an order of magnitude less active but more than an order of magnitude less expensive, then the waste-derived catalyst may be a viable alternative, especially if there is a cost associated with CO₂ emissions that can be included in the economic assessment. Unfortunately there are few life cycle analysis/assessment (LCA) studies available in terms of waste-derived catalysts. Xiao et al. [10] have used LCA to introduce the concept of a “Catalyst Sensitivity Index to provide a measurable index as to how efficiency or performance enhancements of a heterogeneous catalyst” will impact fuel utilization and greenhouse gas emissions for several fuel production and conversion processes in an attempt to quantify the decision making process. This index was highest for gas-to-liquid and coal-to-liquid processes, and negligible for algae transesterification and hydrogenation processes. Frazier et al. [11] completed a LCA of biochar versus metal catalysts for syngas cleaning. Their study indicated that significant greenhouse gas emission reductions and energy savings (93% and 96%, respectively) could be achieved in the production of biochar-based catalysts compared to the conventional alumina-based nickel catalysts. In particular, switch grass grown on marginal lands without fertilizer would be most beneficial for the feedstock considering that twice as much biochar catalyst was required relative to a Ni/Al₂O₃ catalyst to clean the same quantity of syngas.

Biochar is produced from renewable resources, such as switch grass mentioned above, but the production requires energy. The low carbon content (often less than 50% of which only a fraction is fixed carbon) of biomass necessitates significantly larger quantities of feedstock, which coupled with the low density of biomass, produces more emissions for the transportation from source to the processing plant. These considerations must be factored into the economic calculations. In addition to syngas cleaning, biochar-based catalysts have been developed and tested for biodiesel production, and Fischer-Tropsch synthesis [12]. The interaction between the carbon support with the active metals (e.g., Fe) and/or reactants (e.g., tar components) was found to be beneficial but catalysts derived from biochar tend to be less active with lower abrasive resistance compared to the currently available commercial catalysts.

As spent catalysts have higher concentrations of metals (a few %) compared to the primary ores from which the metals were originally extracted (a few ppm), recovery and reuse appears to be an attractive option [13]. Spent petroleum catalysts are treated chemically or microbially to recover the metals, regenerated and reused, or disposed through landfilling. The last option represents an economic loss as well as a potential environmental hazard, while the recovery option requires harsh treatments. A better option may be to reuse the spent catalysts in a different process. For example, spent oil-refining catalysts, which contain rare earth elements and metals such as nickel and vanadium, have been reused at the lab scale for fuel synthesis from biomass, conversion of plastics into fuels, and zeolite production [3].

As the brief review above indicates, there are multiple approaches to improve sustainability. Our group has investigated

the preparation of catalysts and adsorbents from different waste sources including petroleum coke, agricultural wastes, biosolids, and spent catalysts, and renewable sources such as switch grass to provide sustainable alternatives for hydrotreating and gasification. The following sections describe this work and the challenges of using non-pure feedstocks.

2. Porous carbon development

As mentioned above, waste materials generally cannot be used directly but require processing before they can be used as catalysts or adsorbents. For carbon-based materials this processing is usually referred to as activation, and involves increasing the porosity and/or stabilizing the structure by removing volatile species. If the activation step requires too much energy and/or the yield is too low, the economic and/or environmental benefit of using a sustainable and/or waste material will be negated.

2.1. Catalysts from petroleum coke

To upgrade heavy oil and bitumen, hydrogen is added and carbon is rejected – this rejected carbon is called petroleum coke (petcoke). Some petcoke is used as a fuel to produce steam but considerable quantities (millions of tons per year) are stockpiled. As with the byproducts of steel manufacturing (i.e., slag), petcoke is an inexpensive, abundant and available resource for catalyst production. Catalysts are used throughout the upgrading process to convert the recovered petroleum into valuable commercial products such as diesel and gasoline. The majority of our work has been done with petcoke produced by a delayed coking process, and thus in this paper, the term “petcoke” refers to delayed coke, while the term “fluid coke” will be used if the petcoke was produced by a fluid coking process.

Petcoke is a non-porous (surface area < 10 m²/g) solid containing carbon (~78–85%), hydrogen (2–4%), nitrogen (1–2%), sulphur (1–8%), and oxygen (4–5%), as well as silicon, aluminum, titanium, iron, calcium, magnesium, sodium, potassium, phosphorous, and various trace elements in the ash [14]. Although the rich composition, in particular the high sulphur content, limits the applications for this material, these contaminants could act as promoters in a catalytic system or be benign if used with feeds that contain similar components such as in the hydrotreating of heavy oil. In order for the reactants to reach the active sites and minimize coke formation, hydrotreating catalysts require mesoporosity (pores between 2 nm and 50 nm) [15] and, thus, petcoke must be activated to create this porosity if it is to be used as a catalyst support.

Activation is a form of gasification in which part of the carbon structure reacts with an oxidizing agent to create pores within the material. Whereas in gasification the goal is to consume as much of the carbon as possible, in activation, the goal is to create the required porosity but still have a reasonable yield of solid porous carbon. For physical activation, the carbon is exposed to gas phase oxidants such as steam or carbon dioxide. In chemical activation, the carbon is mixed with a chemical agent such as potassium hydroxide, sodium hydroxide or phosphoric acid. Chemical activation is faster but generates a liquid waste stream, as the product must be washed after the activation to remove excess chemicals blocking the pores.

Both the gasification and the activation of carbon have been studied for many years but because every carbonaceous feed behaves differently – petcoke is different than coal, hardwoods, softwoods, grasses, etc. – there are no general rules for predicting gasification rates or activation behavior. Thus, we investigated a number of processing parameters, including flow rate, particle size, and pretreatment, after an oil company (Suncor Energy Inc.)

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