

Silicon carbide coated granular activated carbon: a robust support for low temperature aqueous phase oxidation catalysts

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One of the most attractive features of activated carbon as a catalyst support is its relatively high surface area ($\approx 2,000 \text{ m}^2/\text{g}$) as compared to more traditional ceramic support materials ($20\text{-}250 \text{ m}^2/\text{g}$). Workers in our laboratory have exploited this property in the preparation of extremely active carbon supported bimetallic noble metal catalysts for the deep oxidation (mineralization) of aqueous organics [1-6]. Noble metal loadings of up to 25% by weight have been achieved. Using these catalysts in continuous fixed bed reactors, the complete destruction of typical aqueous contaminants such as alcohols, ketones, organic acids, phenols, aromatics, halocarbons, and jet fuel, in concentrations between 10-200 mg/L, has been demonstrated at the relatively low temperatures between 60-160°C, and pressures to 6 atmospheres. Inorganic products of the oxidation reactions include: CO_2 , H_2O , N_2 , and SO_4^{2-} . Total organic carbon (TOC) concentrations in reactor effluents are typically $< 0.1 \text{ mg/L}$.

However, the economic viability of processes based upon these catalysts is limited because of the unacceptably short useful lives resulting from both chemical and physical mechanisms of degradation [7]. Carbon-supported catalysts are mechanically weak and therefore susceptible to attrition if the momentum transport is large for the particular process. In the case of carbon-supported noble metal catalysts used for low temperature aqueous phase oxidation of organic contaminants, the loss of fine particles resulting from mechanical effects can be extremely costly. Carbon-supported catalysts are also susceptible to oxidation. Inorganic carbon values in aqueous phase oxidation reactor effluents are often substantially greater than would be expected from the mineralization of all dissolved organic contaminants.

In contrast, silicon carbide (SiC) is a material which exhibits excellent chemical, thermal, and mechanical stability characteristics. Ledoux and coworkers have found the use of SiC as a catalytic support advantageous in high-temperature gas phase catalytic reactions [8-10]. These workers attempted to prepare a SiC coated monolith with a specific surface area equivalent to that of activated carbon by wash coating activated carbon onto a ceramic honeycomb and then reacting the carbon with gaseous silicon monoxide (SiO) at temperatures between 1100-1400°C, and

pressures between 0.1-1 torr.



However, the morphology of the product SiC was significantly different from that of the original activated carbon. Reduced surface area of the SiC support resulted in catalysts with much lower activities.

This reaction has been recently employed in our laboratory to produce a SiC coating on the surface of the granular activated carbon used to prepare the bimetallic noble metal aqueous phase oxidation catalyst. The reaction was conducted under vacuum ($\sim 500 \text{ mtorr}$) at 1290°C by heating an alumina boat containing a layer of activated carbon on top of a layer of solid SiO for three hours. Production of β -SiC was confirmed by x-ray diffractometry as shown in Figure 1.

The procedure was utilized during two separate runs. In the first run, the activated carbon support material was used; for the second run, a carbon supported catalyst (designated RP-121) prepared using the same activated carbon and containing 20% platinum and 5% ruthenium (by weight) was used. In both cases, an at least partially SiC derivatized surface was obtained. The β -SiC derivatized activated carbon was then impregnated with noble metals to achieve equivalent loadings of platinum and ruthenium as in the RP-121 catalyst.

The longevities and catalytic activities of these two SiC derivatized catalysts were then compared to those of the un-treated RP-121 catalyst. Separate continuous flow tubular microreactors containing 4.5 - 5 grams of each catalyst preparation were

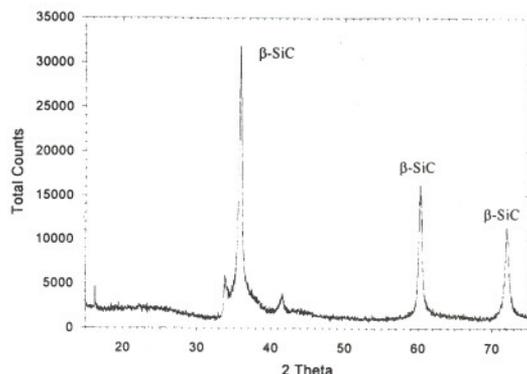


Fig. 1. X-ray diffraction pattern for β -SiC coated activated carbon.

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challenged with influents containing 20 mg/L of aqueous acetic acid. A four fold excess of O_2 was used as the oxidant. The reactors were operated at 130°C and over a range of flow rates corresponding to space times between 20 - 200 seconds. Reactor effluent TOC levels were used to derive pseudo first order rate constants with respect to the organic carbon concentration. The catalyst beds were weighed at the end of each run.

The relationships between conversions (as % mineralization) and reactor space times for the three materials are illustrated in Figure 2. Both β -SiC coated catalysts exhibited roughly equivalent activities toward the mineralization of acetic acid, with pseudo-first order rate constants of $\approx 0.08 \text{ s}^{-1}$, based upon void volume of the bed. These values were higher than that of the untreated catalyst (0.03 s^{-1}). The lower activity for the non-coated catalyst is attributed to extensive loss of catalyst during the experiment. After 200 liters of cumulative flow the RP-121 catalyst bed retained only 54.7% of its original mass. In comparison, the catalyst prepared from the SiC derivatized raw support retained 77.9% of its original mass, and the SiC derivatized RP-121 retained 88.1% of its original mass.

These results unequivocally indicate the potential benefits of the β -SiC coating process with respect to both catalyst activity and longevity. However, the conditions under which the SiC surfaces were prepared on the activated carbon support were far from optimal, and the lack of uniformity in the resulting SiC surface coating was obvious from both visual and microscopic examinations. Further investigation is required to develop methods for the preparation of uniform SiC coatings, and for the variation and control of coating thicknesses.

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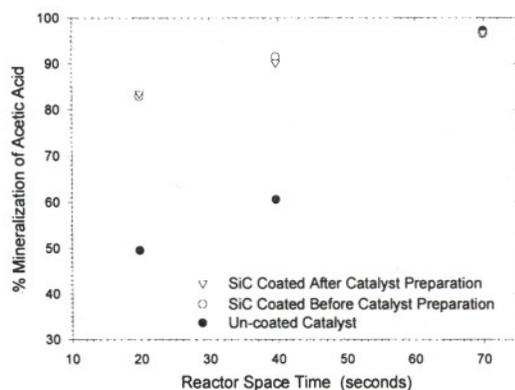


Fig. 2. Mineralization versus reactor space times for β -SiC coated and uncoated catalyst.

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