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**OXIDATION OF BENZENE IN THE AQUEOUS PHASE OVER A
BIMETALLIC CARBON SUPPORTED CATALYST**

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Abstract

Aqueous phase heterogeneous catalytic oxidation of benzene by dissolved oxygen is reported. Using a bimetallic platinum-ruthenium catalyst supported on a high surface area activated carbon, good conversions were obtained at temperatures above 100°C and space-times greater than 40 seconds. Complete conversion of benzene to carbon dioxide and water was achieved at 100°C with a reactor space-time of 300 s.

Keywords: Benzene, oxidation, aqueous phase

INTRODUCTION

The liquid phase deep oxidation of several classes of aqueous organic contaminants has been demonstrated at comparatively mild temperatures between 90-130°C, and pressures between 2.3-6 atm in fixed-bed reactors using dissolved oxygen over a carbon supported platinum-ruthenium catalyst [1-5]. Here we report the oxidation of benzene, an important soil and groundwater contaminant, originating predominately from faulty underground petroleum storage facilities.

EXPERIMENTAL

The Pt-Ru/C catalyst consists of 20% platinum and 5 wt.% ruthenium supported on a high surface area activated carbon (Barnebey-Sutcliffe 580-26). The catalyst was prepared by direct impregnation of the substrate using ruthenium(III) chloride dissolved in 15% HCl, followed by impregnation of platinum using aqueous hexachloroplatinic acid. At each stage the noble metals were reduced under hydrogen at 350°C for two hours, followed by a four hour nitrogen purge at ambient temperature. Details of the catalyst preparation procedure have been given elsewhere [1,3]. BET surface areas of 1760 m²g⁻¹ and 1320 m²g⁻¹ were determined for the untreated substrate and the bimetallic catalyst, respectively. The resulting pore size distribution is illustrated in Fig. 1.

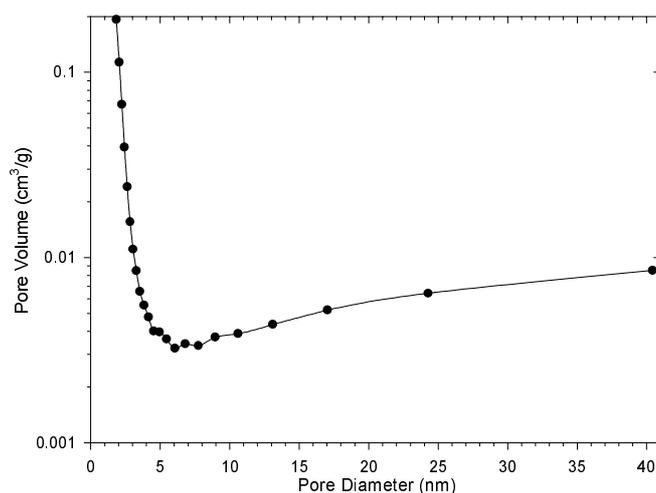


Fig. 1. Pore size distribution for the bimetallic Pt-Ru/C catalyst

Aqueous phase catalytic oxidation experiments were conducted using a pressurized plug flow micro-reactor containing a 4.5 cm³ catalyst bed with a 0.28 fractional void volume. Sufficient pressure was applied to maintain single phase flow. The reactor feed stream was oxygenated using a membrane permeator comprised of non-porous polydimethylsiloxane hollow fibers. The permeator was appropriately size to facilitate the equilibration of pressurized

oxygen gas on one side of the membrane with the aqueous phase feed stream on the other. Inlet oxygen partial pressures were in sufficient stoichiometric excess to result in zero order kinetics with respect to the oxidant. The fixed-bed reactor was fed an aqueous stream consisting of 0.128 mM benzene dissolved in de-ionized water. The reactor was operated over a range of temperatures between 90-120°C. Flow rates were varied to achieve a range of reactor space-times between 10 and 90 s. Effluent benzene concentrations were determined by gas chromatography. In some experiments Total Organic Carbon (TOC) was also monitored using a UV-persulfate-NDIR based analyzer.

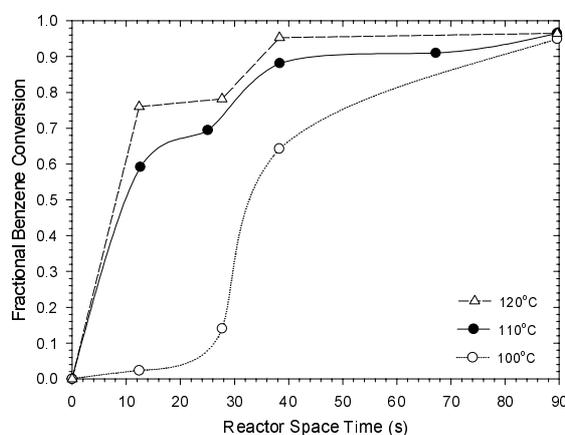


Fig. 2. Benzene conversions for Pt-Ru/C catalyst vs reactor space-time at temperatures between 100-120°C

RESULTS AND DISCUSSION

Adsorption of benzene by the activated carbon support remained significant over the full range of reaction temperatures. At 130°C, the 0.128 mM aqueous feed resulted in an equilibrium sorption capacity of 25 mg g⁻¹. Because of the strong affinity between the catalyst support and the dissolved contaminant, effluent benzene levels for a given set of reactor operating conditions, resulted from a combination of both physical adsorption-desorption by the activated carbon, and the oxidation reactions facilitated by the catalyst. Thus, the reactor operated initially under non-steady state conditions until the catalyst support equilibrated with the aqueous feed stream, after which effluent benzene levels became constant. When increasing reactor temperatures, initially high benzene levels dropped over time to lower steady state levels; when decreasing reactor temperature, the converse was observed.

The reactor was initially operated at 90°C. At this temperature no significant conversion of benzene was observed. At temperatures $\geq 100^\circ\text{C}$ reaction rates became significant. Fractional benzene conversions at temperatures of 100, 110, and 120°C, for reactor space-times up to 90 seconds are presented in Fig. 2. In these experiments the disappearance of benzene in the reactor effluent was monitored by gas chromatography. Reaction products were not identified. The sigmoid character of the relationship between space-time and conversion, most evident at the lowest temperature, prevented the derivation of accurate reaction rate laws. However, by omitting the anomalous data points corresponding to short space-times, pseudo first order rate constants were derived. These are presented in Table 1. These data were also utilized to construct the Arrhenius plot presented in Fig. 3, yielding an estimated Arrhenius activation energy of $\approx 87.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the catalytic reaction. Complete mineralization (deep oxidation) of benzene, as determined by TOC values $< 0.2 \text{ mg/L}$, was achieved at 100°C, using the much longer space-time of 300 s.

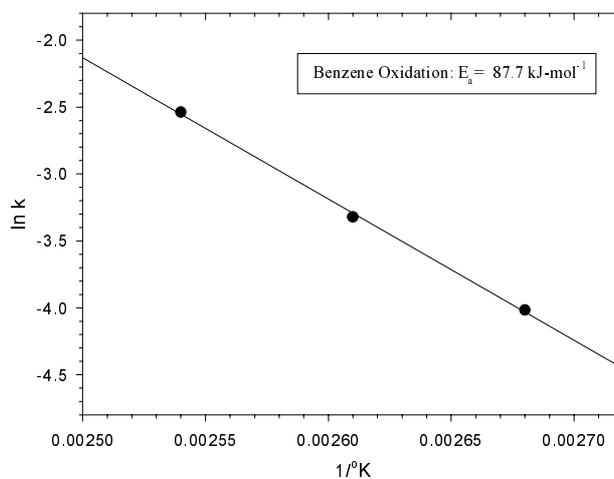


Fig. 3. Arrhenius plot for aqueous benzene oxidation over Pt-Ru/C

Table 1

Pseudo-first order aqueous phase benzene oxidation kinetics over Pt-Ru/C.

Temperature (°C)	Rate constant (s ⁻¹)	Correlation coefficient
90	---	---
100	0.01799	0.8574
110	0.03613	0.9322
120	0.07858	0.9547

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