

# Catalytic benzene coupling on caesium/nanoporous carbon catalysts

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Received (in Bloomington, IN, USA) 24th August 1998, Accepted 19th October 1998

**Caesium/nanoporous carbon materials have a very high affinity for hydrogen, breaking the extremely energetic C–H bond in benzene and promoting its condensation to biphenyl, opening a new class of chemical reactions to heterogeneous catalysis.**

Graphite intercalation compounds of alkali metals have been extensively studied<sup>1</sup> and shown to have very high affinity for hydrogen. The compound C<sub>24</sub>K promotes deuterium exchange with methane<sup>2</sup> and hydrocarbons having acidity equal to or greater than that of benzene.<sup>3</sup> Béguin and Setton<sup>4</sup> found C<sub>8</sub>K could condense benzene to biphenyl at 298 K. However, these materials are pyrophoric, have relatively low surface area, and exfoliate at reaction temperature.<sup>5</sup> In a previous paper<sup>6</sup> we revealed caesium entrapped in high-surface-area (~1000 m<sup>2</sup> g<sup>-1</sup>) nanoporous carbon is an excellent catalyst for double-bond migration in olefins but, unlike alkali-metal graphite intercalation compounds, is not pyrophoric and is thermally stable towards desorption up to 773 K.

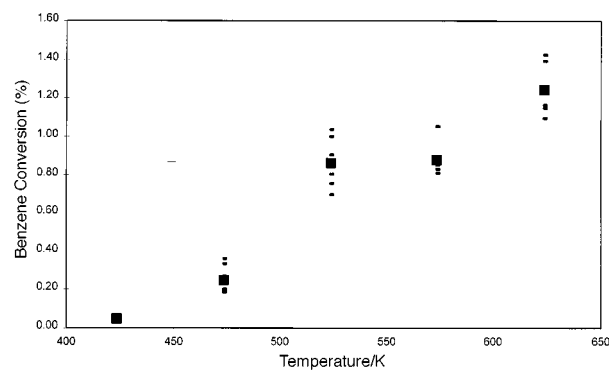
By preparing nanoporous carbon (NPC) from poly(furfuryl alcohol)–poly(ethylene glycol) mixtures<sup>7–10</sup> we obtain chemically inert solids that contain nanopores,<sup>7,8</sup> with sizes distributed around 0.5 nm, and transport pores<sup>11</sup> with sizes distributed around 10 nm that allow access to catalytic sites contained by the nanopores.<sup>12</sup> Since caesium's atomic diameter (0.48 nm covalent) is close to the mean nanopore size of the NPC, the vapor of elemental caesium is rapidly and strongly adsorbed.<sup>6</sup> By this means we have produced materials containing up to 42% caesium by weight.

Through magnetic-susceptibility measurements and electron-paramagnetic-resonance spectroscopy studies<sup>6</sup> of these Cs/NPC materials, we have shown them to contain unpaired electrons. Significantly, an identical *g* factor value of 2.0026 was obtained<sup>†</sup> both for the free radicals in the carbon precursor, as well as those present in material loaded with 15% Cs by weight. The *g*-shift is roughly proportional to the mean spin-orbit coupling constant, which in the case of caesium should be large. The EPR data, however, are not indicative of such an effect. Instead the *g*-value demonstrates that caesium's orbitals do not participate; hence, the electrons from caesium are donated to the carbon. These two facts, along with their demonstrated ability to promote the double-bond migration in olefins,<sup>6</sup> suggest that the Cs/NPC materials should have an affinity for hydrogen similar to, or higher than, their purely graphitic analogues. In 1976, at least two studies<sup>3,4</sup> found that potassium graphite would couple benzene to biphenyl. Béguin and Setton<sup>4</sup> found that a proton donor/acceptor solvent (THF) was required to promote the reaction and that water was required to extract the biphenyl product from the alkali-metal graphite. Matsuzaki and coworkers<sup>13</sup> performed a detailed study of the polymerization of benzene over alkali-metal graphite compounds. Based on a series of experiments, they proposed a polymerization mechanism: two benzene radical anions C<sub>6</sub>H<sub>6</sub><sup>•-</sup> form, then couple and lose dihydrogen forming C<sub>12</sub>H<sub>10</sub><sup>2-</sup> the dianion of biphenyl, a species they observed by Raman spectroscopy. This dianion loses an electron to produce the biphenyl radical anion,

C<sub>12</sub>H<sub>10</sub><sup>•-</sup>, which reacts with another benzene radical anion to propagate the chain and to produce polyphenyl. Finally, caesium metal alone, when reacted with benzene in THF and then washed with water, yielded 1,1',4,4'-tetrahydrobiphenyl.<sup>14</sup>

In our study, batch reactions<sup>‡</sup> of benzene over a 10% Cs/NPC produced biphenyl and terphenyl products. Fig. 1 displays results of several experiments at various temperatures. From these data the apparent first-order activation energy can be calculated as 34 kJ mol<sup>-1</sup>, indicating a coupling-limited, free-radical reaction or that the reaction is taking place in the internal diffusion limited regime. Table 1 displays the typical carbon selectivity. Gas chromatography measurements of the vapor phase over the products confirmed the presence of hydrogen. Control experiments using pure NPC produced no detectable biphenyl. Finally, long-term experiments (8 g benzene reacted over 0.5 g 10% Cs/NPC at 450 °C for 72 hours) confirmed the catalytic nature of the reaction, by achieving over 5 turnovers, based on the *total* molar caesium content.

To confirm the catalyst is not some form of caesium metal that has leached into the liquid phase, we performed a second set of experiments (Table 2), in which benzene was converted to biphenyl in the vapor phase. A mixture of benzene in argon (5 mol%) was circulated over the catalyst at 450 °C and 2 bar.§ By means of a continuous separation built into this recirculating reactor, nearly 100% selectivity to biphenyl was achieved at



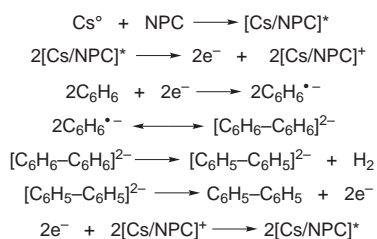
**Fig. 1** In each experiment 8 g benzene was reacted for three hours over 0.5 g of a 10% Cs by weight catalyst: (—) indicates individual experiments, (■) indicates average for a given temperature.

**Table 1** Average carbon selectivity of reaction at 1–3% conversion of benzene

Product	Carbon selectivity (%)
Biphenyl	75
<i>o</i> -Terphenyl	4
<i>m</i> -Terphenyl	7
<i>p</i> -Terphenyl	14

**Table 2** Results of vapor-phase study

Benzene charge/ml	Catalyst/g	Cs <sup>0</sup> in catalyst (%)	Benzene conversion (%)	Cs <sup>o</sup> turnovers	Time/h
100	1.5	15.0	2.40	20.43	96
50	1.0	14.9	2.60	16.70	72
50	1.1	15.8	2.75	15.15	72
50	1.0	0.0	0.00	—	96

**Scheme 1** Plausible catalytic mechanism.

near 2.5% benzene conversion. In this manner 29.8 mmol of benzene were converted to biphenyl in 96 hours over 1.46 mmol of caesium supported on NPC. This amounts to more than 20 turnovers based upon the *total* molar caesium content of the catalyst. The experiment was repeated twice with essentially the same result. Again, a control experiment using pure NPC did not produce detectable levels of biphenyl.

Since Cs/NPC can facilitate the breaking of the C–H bond in benzene (460 kJ mol<sup>-1</sup>), we conclude that the metal provides, through its powerful electropositive nature, the electrons necessary to initiate the process. The carbon mediates the reaction by acting as the electron repository, stabilizing the intermediate radical anions. In the mechanism proposed by Matsuzaki and coworkers,<sup>13</sup> hydrogen and electron transfer are critical steps. The carbon may aid in these steps by promoting the net redox chemistry. Protons generated in the reaction can couple to produce dihydrogen with the carbon supplying the electrons to mediate the process. Additionally, the electron exchange between neutral benzene and the radical anion is facile ( $E_a \approx 12$  kJ mol<sup>-1</sup>),<sup>15</sup> and the carbon may stabilize the intermediate radical anions produced in this chemistry, making the net chemistry catalytic rather than stoichiometric. A plausible catalytic mechanism is shown in Scheme 1. Since the EPR measurements indicate caesium promotes its electron into the local carbon structure, in essence NPC acts as a macro radical anion that may be thought of as [Cs<sup>+</sup>/NPC<sup>-</sup>]. From this vantage point we can begin to see why the material may be so able to promote demanding redox chemistry.

Finally, we have previously shown that caesium, when loaded at high ratios (2/1 Cs<sup>0</sup>/C w/w), promotes the rearrangement of the amorphous NPC to nanotubes, polyhedra and other crystalline structures;<sup>16</sup> transmission electron microscopy<sup>¶</sup> of the catalyst before and after benzene treatment indicates that approximately 5% (by volume) of the carbon has transformed to ordered structures. This limited conversion of the amorphous NPC as compared to previous work<sup>16</sup> may be attributed to the combined effects of lower caesium content and the competitive reaction with benzene. In conclusion, since the phenyl radical anion is extremely difficult to produce and especially considering that deuterium exchange with methane has been shown,<sup>2</sup> these results indicate an entirely new class of radical chemistry may be open to heterogeneous-catalytic exploration in the future.

## Notes and references

† EPR experiments were performed on a Bruker ER-200D electron-paramagnetic-resonance analyzer at 298 K. The authors wish to thank Dr. Paul Krusic and Mr. Steven Hill of the DuPont Company for their assistance with these measurements.

‡ Batch reactions were performed in a stainless-steel, 'tubing-bomb' reactor (2.54 cm o.d., 1.77 cm i.d. 15 cm long, capped with a hex nut and plug, internal volume: 12 cm<sup>3</sup>). Catalyst and benzene were loaded in an argon-atmosphere glove box. Extreme care was taken to eliminate air and water contamination of the experiment. The reactor was sealed with a titanium gasket, removed from the glove box and placed in a fluidized sand bath maintained at the reaction temperature. After the desired reaction time was reached, the reactor was quenched in water and the products were analyzed by gas chromatography, confirmed by mass spectrometry.

§ A recirculating vaporizer/condenser reactor was constructed for the experiments. Catalyst was loaded in an argon atmosphere glove box. Extreme care was taken to eliminate air and water contamination of the experiment. Argon cycled through the system at 1500 sccm in the following order: bubbled through a temperature controlled (298 K) vessel containing 100 ml of benzene that was dried and deoxygenated over molecular sieves and lithium ribbon; the benzene rich (5 mol%) argon passed through a flow controller, a diaphragm pump and to the catalyst bed; the stream was heated to 723 K and flowed through the catalyst bed (1.5 g of catalyst containing 15% by weight Cs, 0.025 s per pass contact time); the reacted stream then returned to the bottom of the benzene vessel in which the biphenyl was trapped due to its low vapor pressure (0.005 bar at 298 K) to repeat the cycle. Products were analyzed by gas chromatography. No terphenyl was detected.

¶ The control (untreated catalyst) and benzene treated samples were prepared for transmission electron microscopic (TEM) studies by depositing them dry on carbon-coated Cu TEM grids. The grids were examined in a JEOL 2000FX S/TEM fitted with a Noran energy dispersive spectroscopic elemental analyzer. The control sample consisted of disordered appearing carbon with the Cs dispersed uniformly throughout the support. While we were not able to image individual particles of Cs on the carbon support, elemental analysis confirmed the presence of Cs everywhere in the sample. The used catalyst appeared similar to the control sample in microstructure as well as elemental composition with the Cs dispersed uniformly throughout the support. However, we observed a small fraction of the carbon to have ordered to graphitic nanoparticles and microscopic sheets of graphitic/turbostratic carbon during the benzene reaction process. No Cs was detected in these ordered pockets of carbon. Based on the TEM analysis, we estimate the amount of ordered carbon in the benzene-treated sample to be approximately 5% on a volume basis.

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Communication 8/06604C