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Oxidized caesium/nanoporous carbon materials: solid-base catalysts with highly-dispersed active sites

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By vapor depositing Cs metal on nanoporous carbon materials and then oxidizing, a solid-base catalyst is produced that is quite active for the aldol condensation of acetone to isophorone.

In previous work we have shown that Cs/NPC materials are very powerful base catalysts.[1] The materials prepared from vapor deposition of elemental Cs provide a greater than 9:1 ratio of the less stable *cis*-but-2-ene over the *trans* isomer in the isomerization of but-1-ene at 273 K. They have a strong affinity for hydrogen,[2] since they can cleave the energetic C–H bond in benzene to promote condensation to biphenyl. Therefore, we sought to explore the activity of the oxidized state of Cs/NPC as a catalyst.

By preparing nanoporous carbon (NPC) with methods discussed previously,[1–4] we obtain high carbon solids that contain nanopores[3,4] with dimensions narrowly distributed around a mode of 0.5 nm and transport pores[5] with dimensions near 10 nm. These transport pores are *critical* for access to the catalytic sites contained in the nanopores.[6] Into these nanopores, the vapor of elemental caesium is rapidly and strongly adsorbed in a highly dispersed state.[1] The resultant materials are paramagnetic,[1] and EPR measurements[2] indicate that electrons of Cs are donated to the carbon. Since the Cs is atomically dispersed within the nanopores, oxidation should yield basic sites that are highly dispersed throughout the carbon. In contrast, aqueous impregnation of Cs salts will lead to large crystallites formed within the macro- and meso-pores.

Utilizing X-ray diffraction as a structural probe, upon exposure of the Cs/NPC to air we find a set of sharp lines superimposed upon the broad background of NPC (Fig. 1). These lines are consistently produced by air exposure of samples prepared in the range of 10–15 wt.% Cs. The lines do not correspond to those exhibited by the various Cs oxides, hydroxides or carbonates whose powder X-ray patterns are well known. It is interesting that when the Cs level is raised to 65 wt.% and the sample is air exposed, the X-ray pattern consists of just four sharp lines at 2θ = 13.05, 26.19, 39.72, and 53.88° (Cu-Kα radiation, λ = 0.15406 nm), corresponding to *d*-spacings of 6.781, 3.400, 2.267, and 1.700 Å, respectively, indicating that a crystalline form of Cs hydrous oxide has formed.[7] It is plausible that the X-ray pattern for air exposed Cs/NPC prepared at the lower loading of Cs corresponds to an intermediate hydrous oxide structure.

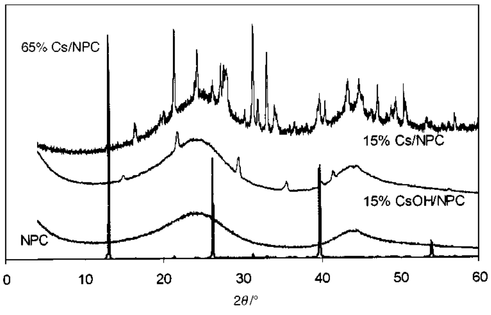
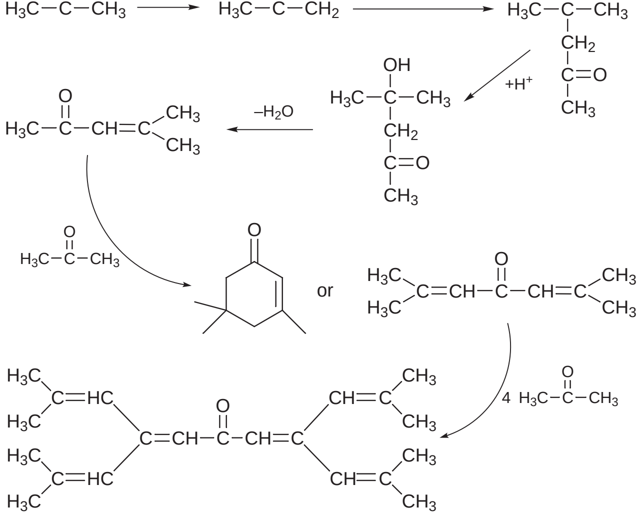


Fig. 1 Scaled XRD plots of NPC, 15% Cs on NPC, 65% Cs on NPC and 15% CsOH on NPC. Radiation used was Cu-Kα (λ = 0.15406 nm).

To determine if this oxide of vapor-deposited Cs on NPC led to a different level of activity than that obtained by impregnation with an aqueous salt, we chose to study the base-catalyzed aldol-condensation of acetone. Starting with Cs/NPC, this reaction would be expected to rapidly oxidize the Cs/NPC *in situ*, since water is a by-product of the coupling steps. Secondly, since the condensation products may react further to produce higher molecular weight species, inclusion of transport porosity within the carbon support should be critical to avoid rapid catalyst deactivation.

The liquid phase isophorone process[8] operates at 6–10% acetone conversion with a sodium hydroxide catalyst, an isophorone yield around 70% and losses due to heavies production. A more energy-intensive, vapor-phase process is also employed in which the acetone is passed over solid oxide type bases. Both processes incur a great deal of separations costs, requiring as many as four distillation columns operating under vacuum to reduce further by-product formation. In 1995, isophorone sold for $4+/lb and the sole United States supplier was Union Carbide. The total world capacity was ≈156 MM lb./yr. Isophorone's uses range from a high-boiling, low-evaporative solvent for synthetic polymers to an insecticide (when converted to 3,5-xylenol). The fastest growing market for isophorone is as a building block for light-stable polyurethane.[9]

The base-catalyzed condensation of acetone (Scheme 1) begins with the extraction of the acidic α-proton to form the enolate anion, which attacks a second acetone to form the tetrahedral alkoxide ion intermediate, which is protonated to form the aldol. At elevated temperatures the aldol releases water to form mesityl oxide, which can undergo subsequent condensation steps. Upon the condensation of the aldol to form the



Scheme 1 The base-catalyzed, aldol-condensation reaction of acetone.

disubstituted enone, the material may simply form the conjugated diene-one product or the industrially significant, cyclic isophorone. The conjugated nature of the enone product allows for continued additions, forming higher molecular weight species that can accumulate rapidly in an all-nanoporous catalyst, thus restricting access to the active sites within the nanopores and shutting down reaction.

Experiments were carried out in a gas-phase flow reactor.[†] A steady argon flow (150 cm^3 min^{-1}) carried acetone vapor from a room-temperature gas sparger through the heated catalyst bed. Unreacted acetone and the heavier products were condensed and analyzed quantitatively by gas chromatography and mass spectrometry. The major product was isophorone along with mesityl oxides and higher-molecular-weight species that were lumped into a fraction called 'heavies'. Acetone conversion and selectivity to isophorone obtained over the vapor-deposited Cs/NPC catalyst for various temperatures are displayed in Table 1. Acetone conversion and selectivity to isophorone both maximize at 225–250 °C. At 20 °C isophorone selectivity drops due to increased mesityl oxide formation. At temperatures above 250 °C the activity of the catalyst dropped even though the selectivity to isophorone remained high. This was most likely due to the accumulation of heavy products in the pores. Each catalyst dropped to $< 20\%$ of its initial activity within 5 h and gained approximately 10% of its initial weight. At 225 and 250 °C the turnovers (mol of acetone converted/mol Cs) before catalyst deactivation were at a maximum of ≈ 10 (Table 1).

Significantly, the effect of air exposure on the catalyst before reaction was to *increase* its initial activity. Catalyst samples that were not air-exposed before reaction did not produce isophorone in the first hour on stream. After this induction period, however, they behaved as the air exposed samples did.

When compared to catalysts prepared by vapor deposition of elemental Cs, those samples that were prepared with CsOH solution[‡] were less active and less selective. The selectivity to isophorone over the catalyst prepared by vapor deposition was *ca.* 60% throughout the experiment, whereas the selectivity for the solution-impregnated sample began at 45% and declined to 30%. Both materials gained approximately 10% of their initial weight in non-volatile compounds.

The vapor deposition of Cs led to catalysts that maintained their high selectivity to isophorone even as their activities dropped. The selectivity to isophorone remained 60% over a conversion range from 0–20%. As the acetone conversion approached 20% the loss in selectivity due to heavies formation became more significant. Attempts made to achieve higher conversions were not successful since the catalyst deactivated more rapidly due to non-volatile product accumulation.

Finally, as control experiments, we tested the NPC support alone without Cs and a sample of Cs-loaded NPC containing only nanopores.[§] Neither material led to any significant acetone conversion. The Cs on all-nanoporous carbon catalyst, however, did increase in mass by an amount equal to 10% of its initial mass.

The GCMS data obtained indicate that the higher-energy, non-cyclic trimer was the species that led to heavies formation; none of the heavy materials identified contained cyclic fragments. This makes sense since the protons that are active for base extraction are α to the carbonyl or conjugated. The non-cyclic trimer has 12 of these active protons and the isophorone has only 3 that are not sterically hindered. Hence the key to reducing heavies formation and deactivation is to promote ring formation over oligomerization. Since the heat of formation and the activation energy to form the non-cyclic products are higher, a reduction in temperature should favor the isophorone product. Also, ring formation should have a lower (more negative) $\Delta S^{\ddagger}$, therefore, a decrease in temperature should again favor its formation. Secondly, any variable that reduces the overall conversion or catalyst basicity should reduce heavies formation. Thus, less basic metals such as potassium or sodium, lower acetone concentrations in the feed, and shorter contact times in the reactor should favor isophorone production.

Table 1 Conversion, carbon selectivity towards isophorone and Cs^0 turnovers at various temperatures. Argon flow rate: 150 cm^3 mol^{-1} saturated with acetone at 25 °C

T/°C	Conversion (%) (per g Cs)	Isophorone selectivity (%)	Cs Turnovers
200	6.1	54	5.34
225	11.9	61	10.43
250	11.4	60	10.04
275	5.2	57	4.56
300	3.8	57	3.38

Caesium, vapor-deposited into the carbon and then oxidized, is more active than Cs deposited from a salt in aqueous solution. The Cs hydrous oxide that results from oxidation of the vapor-deposited element is certainly a different phase; by examining the X-ray diffraction patterns of the two materials we were able to confirm this. The samples prepared with the CsOH solution showed patterns indicative of large hydroxide crystals. In contrast, the used vapor-deposited Cs/NPC material displayed an X-ray diffraction pattern with sharp lines, but the lines did not match any of the known caesium hydroxides or oxides. This set of results points to a new approach in the synthesis and use of solid Brønsted bases for continuous-flow organic synthesis. By preparing a carbon with both nanopores and mesopores, we can vacuum deposit cesium in a highly dispersed state, convert it to an active form *via* oxidation, and provide the necessary avenues for rapid molecular ingress and egress.

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Notes and references

[†] A Tylan mass flow controller regulated an argon (Matheson Grade) carrier-gas flow. The argon flow served two purposes: to purge the reactor system of air and to carry acetone at its room-temperature vapor pressure from a bubbler to the reactor. The reactor consisted of a ½″ o.d. quartz tube heated by heat tape, the temperature of which was regulated by an Omega PID temperature controller. The catalyst was placed in the heated zone of the reactor between two plugs of glass wool. After leaving the reactor, the acetone–argon stream was cooled and condensed into a catch pot by a shell and tube condenser, through which flowed −10 °C chilled glycol. Samples were taken by removing all the liquid from the catch pot with a syringe inserted through a serum cap, weighed, spiked with a biphenyl standard, and analyzed on a Varian GC with an FID detector.

[‡] A sample of CsOH/NPC was prepared by stirring the NPC with 50% CsOH solution for 1 h, filtering, and vacuum drying at 350 °C for 24 h.

[§] NPC prepared by the pyrolysis of poly(furfuryl alcohol) alone at 850 °C for 8 h under helium produces a purely nanoporous material with no pores larger than 2 nm.

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