Alkali metals on nanoporous carbon: new solid-base catalysts

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Caesium entrapped in nanoporous carbon is not pyrophoric, is thermally stable towards desorption up to 773 K, but retains its ability to produce hydrogen from water, and is a strong basic catalyst, providing 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.

Materials produced from alkali metals and carbon have been of interest to researchers for many years. Graphite intercalation compounds of alkali metals have been extensively studied[1] and shown to be active basic catalysts in reactions such as side-chain alkylation,[2] but-1-ene isomerization[3] and amine synthesis.[4] Unfortunately, these materials were found to be pyrophoric, had relatively low surface area, and exfoliated at reaction temperature.[5] A catalytically active caesium fulleride, $C_{20}Cs_6$, has been reported, but it was found to be highly air-sensitive.[6]

Carbogenic molecular sieves (CMS) are chemically inert solids that contain nanopores,[7,8] formed from aromatic nanodomains, arranged chaotically in space. Here, we show that alkali metals introduced into a CMS structure adsorb in these nanopore spaces, and that curvature effects within the CMS pores provide for a much higher thermal stability, and that these materials are exceptionally active base catalysts in double-bond migration.

CMS samples were prepared pyrolitically from polyvinylchloride–polyvinyldichloride-, poly(furfuryl alcohol)- and poly(furfuryl alcohol)–poly(ethylene glycol) mixtures.[7–10] A poly(furfuryl alcohol)–poly(ethylene glycol) mixture (PFA–PEG) produces material that forms a nanopore structure similar to the PFA carbons, with a pore-size distribution centred around 0.5 nm. However, the addition of PEG results in the formation of transport porosity[11] with a second distribution centred around 10 nm, that allows access to catalytic sites contained in the nanopores.[12] Cs was chosen as the catalytic metal because it is the most electropositive element and its covalent atomic diameter (0.48 nm) is close to the nanopore size of the CMS (*ca.* 0.5 nm). Since Cs is strongly electropositive, a significant portion of the Cs may be ionized (crystallographic diameter 0.34 nm), which should add to the compound's stability.

The synthesis of the Cs/CMS material was achieved by vapour-phase deposition.† The base-catalysed isomerization of but-1-ene to but-2-ene, which begins with the abstraction of the allylic proton to form the *cis* or *trans* form of the allyl anion,[13] was used to probe for catalytic activity. Since the *cis* form of this intermediate is more stable than the *trans* form, *cis*-but-2-ene is formed predominantly in base catalysis, although *trans*-but-2-ene is more stable thermodynamically.

Table 1 Average conversion on 4.5 g catalyst and *cis*/*trans* ratio of the product gas for the isomerization of 15 cm^5 min^{-1} butene to *cis*- and *trans*-but-2-ene at 298 K and 1 bar. Six datapoints (gas chromatography) were collected from the flow reactor over a 2 h period and averaged

Catalyst	Conversion (%)	*cis*/*trans* ratio
3% Cs-PFA–PEG	13%	2.3
10% Cs-PFA–PEG	75%	3.3
11% Cs-PFA–PEG	60%	4.9
18% Cs-PFA–PEG	90%	2.8
21% Cs-PFA–PEG	87%	3.7

Samples containing 3–42 mass% Cs in CMS‡ were synthesized. The thermal stability of these materials was demonstrated by heating them in vacuum to temperatures as high as 773 K; the Cs did not desorb from the CMS. In contrast Cs is lost rapidly from Cs/graphite compounds, which exfoliate readily.[5]

Results of magnetic susceptibility and EPR measurements show a significant population of unpaired electrons exists in these materials. When a 17% Cs/CMS sample was exposed to 100% humidity at 288 K it absorbed 850 mg g^{-1} of water. When submerged in oxygen-free water, a 9.2% Cs sample produced sufficient hydrogen to indicate that 26% of the Cs was still active for water reduction.§ Hence, the Cs is active and accessible. Yet, unlike metallic Cs and graphite Cs compounds, Cs/CMS is not pyrophoric, even at 40% Cs loading.

A wholly nanoporous pyrolized polyvinylchloride–polyvinyldichloride carbon impregnated with 14% Cs showed no catalytic activity for but-1-ene isomerization¶ at 298 K, but did show activity at higher temperatures (18% conversion at 523 K). When transport porosity is added to the CMS, making the Cs in the nanopores more accessible, the reaction took place at low temperatures (Table 1). The catalysts were found to be stable, with a reaction turnover of > 30 (30 mol of but-2-ene produced per mol of Cs) before deactivation. To determine the global, first-order rate constant for the reaction we diluted the butene feed to 33 mol% but-1-ene in argon. From differential conversion experiments¶ on a 9% Cs sample we determined an apparent first-order rate constant (k_a) of 0.07 s^{-1} g^{-1} and a *cis* : *trans* ratio of 9.1 at 273 K. This combination of high bacisity with reduction activity and the lack of pyrophoricity makes Cs/CMS extraordinarily interesting and useful.

Footnotes

† After a sample of the CMS was heat-treated in vacuum at 450 °C for 24 h, Cs vapour was introduced into the carbon at moderate temperature (350 °C) at its vapour pressure (*ca.* 10 mmHg). The temperature was held at 350 °C under static vacuum for 24 h.

‡ Galbraith Laboratories, Inc. provided metal analysis *via* plasma emission spectroscopy for the determination of alkai-metal loading.

§ A 2 g sample of catalyst was submerged in 20 ml of deionized, oxygen-free, water, without exposure to air. Gas evolved. The gas was quantified and determined to be hydrogen by gas chromatography. The water and catalyst were titrated with 0.0125 m sulfuric acid to calculate the amount of Cs present as CsOH.

¶ We constructed a computer-controlled, tubular, flow reactor. For the initial experiments: the reactor was loaded in an inert atmosphere with 4.75 g of catalyst. Technical grade but-1-ene (Matheson gas company) flowed at 15 cm^3 min^{-1} at atmospheric pressure. For the kinetic experiments: the reactor contained 3.0 g of catalyst. Technical grade but-1-ene flowed at 20 cm^3 min^{-1}, mixed with 40 cm^3 min^{-1} argon at atmospheric pressure. Analysis was performed *via* gas chromatography.

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