Side-chain alkylation of toluene with propene on caesium/nanoporous carbon catalysts

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Caesium/nanoporous carbon materials are powerful solid-base catalysts, promoting the side-chain alkylation of toluene with propene in a continuous flow reactor at conditions as mild as 150 °C and 50 psig.

When a strong base, such as Na metal, is employed as a catalyst, alkylation occurs at the benzylic hydrogen of the side chain. During the later 1950s, many researchers[1–5] explored this chemistry, most notably, Pines *et al.*[1,2,4] Recently, there has been much interest in examining novel solid-base catalysts for larger scale reactions such as side-chain alkylation of toluene with methanol[6–9] and olefins.[10,11] To date, however, there are no industrial processes that take advantage of this chemistry to produce alkylbenzenes from lower-cost toluene.[12] As early as 1964 Foster[10] had shown that graphite intercalation compounds of alkali metals readily promoted the side-chain alkylation of toluene with ethylene, but reaction was slow, required high pressure and it was not clear if the alkali metal had remained intercalated in the graphite.

In contrast to the graphite intercalation compounds of alkali metals, which exfoliate readily,[13] we have shown that Cs entrapped in nanoporous carbon is well dispersed and very strongly bound.[14] Preparing nanoporous carbon (NPC) with macropores provides for facile molecular ingress and egress to the catalytic sites.[15]

We have shown that Cs/NPC is active enough to break the C–H bond in benzene (110 kcal mol^{−1}) and to promote its condensation to biphenyl.[16] Given this result, we expected the catalyst to remove the more facile benzylic hydrogen from toluene readily, and if an olefin such as propene were present, to produce *n*-butylbenzene and isobutylbenzene. At the same time in the case of propene, cyclization and release of dihydrogen could lead to the dicyclic products 1-methylindan, 1,2,3,4-tetrahydronaphthalene and 2-methylindan.

Batch, liquid phase reactions† of toluene and propene over this nanoporous carbon catalyst containing *ca.* 10 wt% Cs produced *n*-butylbenzene, isobutylbenzene and 2-methylindan. Table 1 displays the results of several experiments carried out at 150 °C and at various conversions. The major product was isobutylbenzene. Propene was the limiting reactant in all these experiments. Once the propene was consumed, secondary reactions began to become important. As was the case in the reaction of benzene over Cs/NPC,[16] aromatic-ring coupling produced species such as bibenzyl, dimethylbiphenyls, and methyldiphenylmethanes. Additionally, cyclization of iso-butylbenzene produced 2-methylindan. If 1-methylindan and 1,2,3,4-tetrahydronaphthalene were produced, they remained below our detection limits. Both side reactions should produce H_2 and GC measurements of the vapor phase over the products confirmed that H_2 indeed had been produced. Control experiments using carbon without C_2 produced no detectable reaction. At higher conversions, the catalyst achieved over nine turnovers based on the total moles of Cs, a lower limit value that confirms the catalytic nature of the reaction.

In a second set of experiments, to avoid the possible complication of Cs leaching into the liquid phase, toluene was converted to butylbenzenes in the vapor phase using a tubular flow reactor. A mixture of toluene in propene (5 mol %) was circulated over the catalyst at temperatures from 150–400 °C and 4 bar,‡ (Fig. 1, Table 2). The increase in the availability of propene reduced the toluene coupling to an undetectable level. Propene coupling, however, did occur with the excess propene in the system to form C_6 compounds such as 4-methylpentene, cyclohexane, hex-1-ene and dimethylbutenes. Above 150 °C, *ca.* 10% of the propene that reacted went to the C_6 products, indicating the potential utility of Cs/NPC as a catalyst for producing higher-molecular-weight olefin monomers. This propene coupling may also account for the decrease in activity at > 250 °C. At 350 and 400 °C the catalysts gained mass (3.6 and 6.0% of their initial mass, respectively). This suggests that deactivation arose due to the formation of propene oligomers in the pores, resulting in a loss of diffusive transport to the catalytically active sites. The sample of catalyst used at 400 °C not only gained mass, but also was coated with a hexane-soluble, waxy film.

We find that Cs/NPC yields high iso/normal butylbenzene ratios ($\geqslant$10). This indicates that the predominant mechanism proceeds *via* surface anions and through the formation of the benzyl anion from the toluene substrate. Pines and Stalick[17]

Table 1 Results of batch study[a]

Conversion (%)		Toluene selectivity (%)				Turn-over
Toluene	Propylene	Coupled	Isobutyl	*n*-Butyl	Indan	
0.03	0.40	0.00	100.00	0.00	0.00	0.039
0.12	1.41	0.00	82.99	0.00	17.01	0.137
1.03	18.84	0.44	70.44	9.17	19.94	2.367
1.06	18.35	0.55	72.47	9.83	17.14	2.452
3.49	38.19	1.29	70.23	13.76	14.72	3.934
6.82	$\approx$100.00	2.49	71.66	13.16	12.69	10.657
7.12	$\approx$100.00	3.19	73.11	11.95	11.75	9.274

[a] Conversion of toluene and propylene and selectivity were calculated from GC of the liquid phase. Turnovers were calculated by titrating the used catalyst for Cs content with H_2SO_4. All products were identified by GCMS.
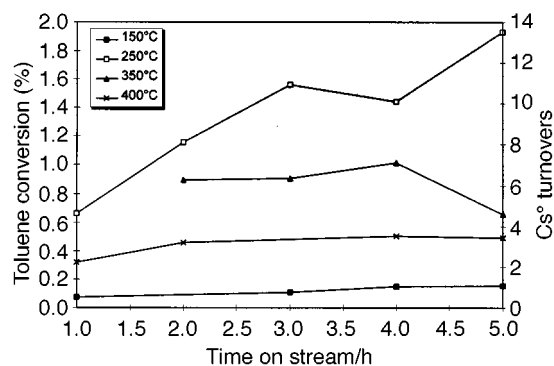

Fig. 1 Vapor-phase conversion and catalyst turnovers *versus* time on stream at 4 bar gas pressure (5% toluene in propylene) and temperature. Conversion of toluene, was calculated from GC of the liquid phase. Turnovers were calculated by titrating the used catalyst for Cs content with H_2SO_4.

Table 2 Results of gas-phase, continuous experiments[a]

		Toluene selectivity (%)				
T/°C	Propene selectivity	Isobutyl-benzene	n-Butyl-benzene	Methyl-indan	Tetra-hydro-naph-thalene	Catalyst weight gain (%)
150	100.0	94.7	2.6	2.7	0.0	<0.1
250	89.4	72.3	8.2	15.8	3.6	<0.1
350	93.0	79.8	7.6	10.7	1.9	3.6
400	93.5	85.5	9.6	5.0	0.0	6.0

[a] Propylene selectivity to alkylation products was calculated by comparing the amount of propylene converted to C_6 byproducts to the toluene conversion. Conversion and selectivity of toluene, were calculated from GC measurements of the liquid phase. Products identified by GCMS.
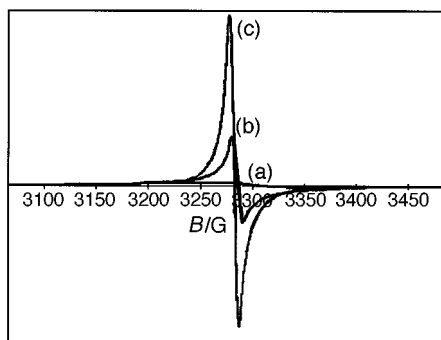
Fig. 2 EPR differential plot of: (a), carbon precursor; (b), carbon loaded with 30% Cs; (c), carbon loaded with 3% Cs.

have shown that a large normal to iso ratio is the best indicator of an anionic rather than free-radical mechanism.

That the chemistry over Cs/NPC should proceed through anions rather than radicals makes good sense based on characterization of the Cs/NPC by EPR spectroscopy. Our EPR measurements (Fig. 2) show the existence of such radical anions, and the measured g-value of 2.0026[16] indicates that the unpaired electrons are transferred from the Cs to the carbon. The EPR spectra also show that more unpaired electrons are present at low Cs levels (3 wt%) than at high loadings (30 wt%). Previously, we found that the electronic character of the material goes from strongly paramagnetic to weakly paramagnetic and diamagnetic with increased Cs content.[14] This transformation arises from spin pairing within the polyaromatic nanodomains as additional electrons are added. Based on these results, at the intermediate Cs loadings (10 wt%) used for the catalysts examined here, the material should behave as much, or more, like a Lewis base than as a radical. We conclude that radical anions, represented as $Cs_n/NPC^{n-\cdot y\cdot S}$ where $y = [1 +$

$(-1)^{n+1}]/2$, and the corresponding spin-paired multiply charged anions (formed by addition or removal of one electron) catalyze this reaction and drive the chemistry toward iso-butylbenzene formation. The same intermediate anions which produce isobutylbenzene also can react intramolecularly to form the corresponding bicyclic compounds and also through an anion mechanism.

In conclusion, we have shown the Cs/NPC materials to be powerful Lewis bases which promote the side-chain alkylation of toluene at unprecedentedly mild conditions.

Notes and references

† 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 valve assembly, total internal volume: 15 cm). Catalyst and toluene were loaded in an argon-atmosphere glove box. The reactor was sealed with a titanium gasket, removed from the glove box, charged with propene and placed in a fluidized sand bath maintained at the reaction temperature.

‡ A recirculating vaporizer/condenser reactor was constructed for the experiments. Propene (maintained at 4 bar with live feed) cycled through the system at 1500 sccm in the following order: bubbled through a temperature controlled (298 K) vessel containing 100 ml of toluene; the toluene rich (5 mol%) propene passed through a flow controller, a diaphragm pump and to the catalyst bed; the stream was heated to reaction temperature and flowed through the catalyst bed (1.5 g of catalyst containing 10 wt%/Cs 0.025 s/pass contact time); the reacted stream then returned to the bottom of the toluene vessel to repeat the cycle.

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