

Selective Synthesis of Ethylbenzene and Styrene by Cross-coupling between Toluene and Methane over a Lithium-promoted Y_2O_3 -CaO Catalyst

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Isotope-labelling experiments have shown that toluene oxidative methylation using methane to form C_8 hydrocarbons over a lithium promoted Y_2O_3 -CaO catalyst involves a cross-coupling between the methyl and benzyl radicals on the surface.

It is generally accepted that the mechanism of oxidative coupling of methane to C_2 hydrocarbons involves formation of methyl radicals and their subsequent dimerization.¹ We have recently reported the oxidative cross-coupling reaction between methane and toluene to form ethylbenzene and

styrene, using lithium promoted MgO and Y_2O_3 -CaO catalysts,² which are effective catalyst systems for the methane coupling reaction.³ In contrast, little has been known of the mechanism of cross-coupling between methane and the hydrocarbons.⁴ We herein report on the mechanism of the cross-coupling reaction based on isotope-labelling experiments using deuteriated toluene.

For the oxidative methane coupling reaction, a decrease in

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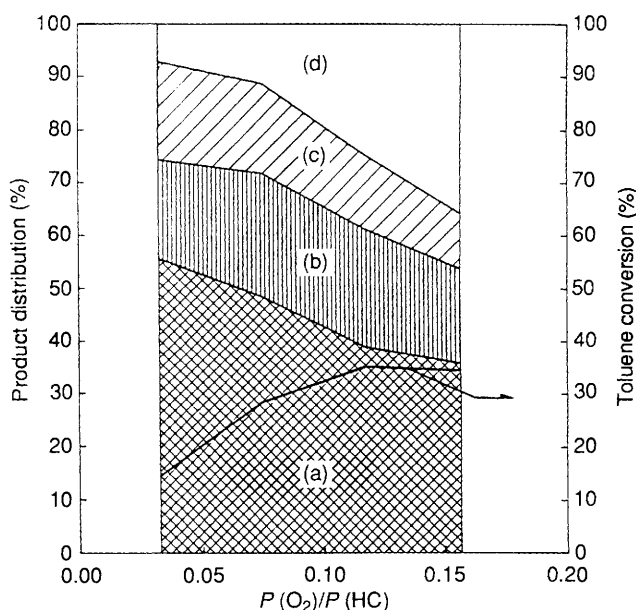


Fig. 1 Effect of the ratio of the partial pressure of oxygen to that of hydrocarbon reactants on the product distribution and the toluene conversion. (a) Ethylbenzene; (b) styrene; (c) benzene; (d) CO_x etc. Catalyst, 3 wt% $\text{Li}_2\text{O}/10$ mol% $\text{Y}_2\text{O}_3\text{-CaO}$, 1.0 g; $T = 973$ K; $\text{CH}_4 : \text{C}_6\text{H}_5\text{CH}_3 = 50 : 2.5$ $\text{cm}^3 \text{min}^{-1}$ NTP

the $P(\text{O}_2)/P(\text{CH}_4)$ ratio results in an increase in C_2 selectivity, indicating that further oxidation of the methyl radical might be substantially suppressed by controlling the oxygen concentration.⁵ Similarly, lowering the $P(\text{O}_2)/P(\text{HC})$ [HC (hydrocarbon), $\text{CH}_4 : \text{C}_6\text{H}_5\text{CH}_3 = 20 : 1$] ratio was found to be effective in improving the selectivity of the cross-coupling, see Fig. 1.[‡] The highest C_8 (ethylbenzene and styrene) selectivity (74.3%) was attained at $P(\text{O}_2)/P(\text{HC}) = 0.032$. It is noteworthy that there were no oxygenated compounds, such as benzaldehyde, benzoic acid or phenol in the product effluent, while complete oxidation to CO and CO_2 was accelerated by increasing the $P(\text{O}_2)/P(\text{HC})$ ratio. The oxygen molecule is effectively utilized for hydrogen extraction from methane and toluene giving the corresponding radicals, not the oxidant.

An interesting feature of this coupling reaction is that an increase in the toluene flow rate results in preferential cross-coupling between methane and toluene compared with the homo-coupling of methane or toluene as shown in Fig. 2. In particular, there is no formation of bibenzyl or stilbene, which are formed in the reaction of toluene with oxygen in the absence of methane.⁶ These results may be closely related to the stability and reactivity of both radicals. Bond dissociation energies of the methane C-H bond and benzylic C-H bonds of toluene are 435.6 and 356.5 kJ mol^{-1} and the heats of formation of methyl and benzyl radicals are 142.3 and 188.7 kJ mol^{-1} , respectively,⁷ suggesting that the benzyl radical is readily formed and relatively less reactive than the methyl radical. Even in the presence of an excessive amount of

[‡] A 3 wt% $\text{Li}_2\text{O}/10$ mol% $\text{Y}_2\text{O}_3\text{-CaO}$ catalyst was prepared as previously described.² The reaction gas mixture, $\text{CH}_4 : \text{C}_6\text{H}_5\text{CH}_3 : \text{O}_2 = 50 : 2.5 : 1.7\text{-}8.1$ $\text{cm}^3 \text{min}^{-1}$ NTP, was fed into a quartz reactor (12 mm i.d.) packed with 1 g of the catalyst at 973 K. The products were analysed on-line by using FID/TCD gas chromatography. Aromatic compounds such as ethylbenzene, styrene, benzene and trace amounts of isopropylbenzene and xylene were detected. Selectivities were calculated on the basis of toluene converted.

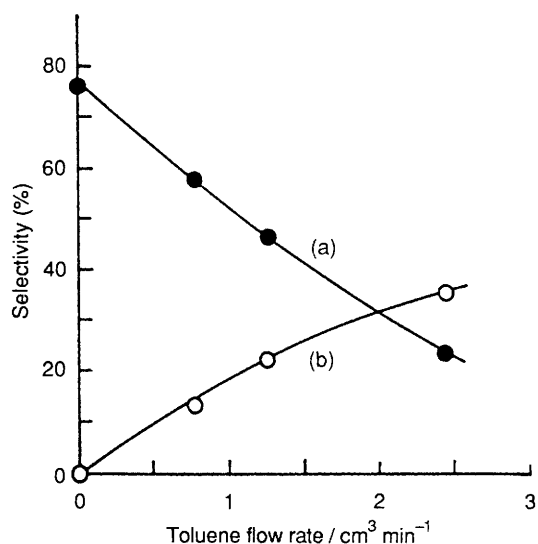


Fig. 2 Effect of toluene flow rate on C_2+ and C_8+ selectivities. Catalyst, 3 wt% $\text{Li}_2\text{O}/10$ mol% $\text{Y}_2\text{O}_3\text{-CaO}$, 1.0 g; $T = 973$ K; $\text{CH}_4 : \text{O}_2 = 50 : 4$ $\text{cm}^3 \text{min}^{-1}$ NTP. (a) C_2+ : ethane, ethylene, propane and propylene; (b) C_8+ : ethylbenzene, styrene, xylenes and propylbenzenes. Selectivities are calculated on the basis of moles methane converted

Table 1 Deuterium distributions in the products of the reaction between CH_4 and $\text{C}_6\text{D}_5\text{CD}_3$ ^a

Compound	<i>m/z</i>	Isotope	Intensity (%) ^b
Ethylbenzene ^c	112	$\text{C}_6\text{D}_5\text{-CDH-CH}_3$	43
	113	$\text{C}_6\text{D}_5\text{-CD}_2\text{-CH}_3$	100
	109	$\text{C}_6\text{D}_5\text{-CH=CH}_2$	65
Styrene	110	$\text{C}_6\text{D}_5\text{-CD=CH}_2$	100
		and $\text{C}_6\text{D}_5\text{-CH=CDH}$	
	111	$\text{C}_6\text{D}_5\text{-CD=CDH}$ and $\text{C}_6\text{D}_5\text{-CH=CD}_2$	40
Benzene	112	$\text{C}_6\text{D}_5\text{-CD=CD}_2$	16
	82	$\text{C}_6\text{D}_4\text{H}_2$	36
	83	$\text{C}_6\text{D}_5\text{H}$	97
Toluene	84	C_6D_6	100
	98	$\text{C}_6\text{D}_5\text{-CDH}_2$	13
	99	$\text{C}_6\text{D}_5\text{-CD}_2\text{H}$	48
	100	$\text{C}_6\text{D}_5\text{-CD}_3$	100

^a Reaction conditions, $\text{CH}_4 : \text{C}_6\text{D}_5\text{CD}_3 : \text{O}_2 = 50 : 2.5 : 4$ $\text{cm}^3 \text{min}^{-1}$ NTP; $T = 973$ K; catalyst = 1.0 g of 3 wt% $\text{Li}_2\text{O}/10$ mol% $\text{Y}_2\text{O}_3\text{-CaO}$. Reaction effluents were trapped by a dry ice-methanol trap system at 195 K. ^b Intensities of the isotopes were measured by field ionization GC-MS. ^c D-position was determined by GC and NMR spectroscopy.

methane, predominant formation of the cross-coupling products suggests that the concentration of the methyl radical generated on the surface is comparable to that of the benzyl radical and that both radicals are combined before reaching the gas phase. Lack of homo-coupling of the benzyl radicals might be due to the relatively low reactivity of the benzyl radicals on the surface.

Isotope-labelling experiments using $\text{C}_6\text{D}_5\text{CD}_3$ under the same reaction conditions also support cross-coupling of both radicals on the surface. Table 1 summarizes the deuterium distribution in three major reaction products along with toluene. The cross-coupled product, ethylbenzene, consists mainly of $\text{C}_6\text{D}_5\text{CD}_2\text{CH}_3$, giving clear evidence for the combination of $\text{CH}_3\cdot$ and $\text{C}_6\text{D}_5\text{CD}_2\cdot$. During the formation of

styrene almost complete H-D scrambling of the alkenic hydrogen of styrene would take place.

Interestingly, the toluene recovered after the reaction contained $C_6D_5CD_2H$ and $C_6D_5CDH_2$. This observation indicates that prior to combination of both radicals a rapid H-D exchange reaction takes place in the methyl group of toluene, which also suggests that the benzyl radical generated is rapidly quenched by a surface hydrogen atom rather than the methyl radicals. In contrast to the behaviour of the benzyl radical, the deuteriated methane recovered is detected as a small amount of CH_3D , with no further deuteration. These results suggest that C_2 formation probably occurs in the gas phase; the mechanistic details will be discussed in a full paper.

Another feature of our coupling reaction is that almost equal amounts of C_6D_6 and C_6D_5H were obtained and there was no formation of biphenyl and $C_6D_5CH_3$. While benzene formation may be interpreted by hydrogenolysis of toluene with hydrogen or disproportionation of toluene into benzene and xylene, these routes would involve phenyl radicals and are ruled out by experimental data which show a lack of multi-deuteriated methane, relatively low concentrations of hydrogen molecules in the gas phase and a small amount of xylene under our reaction conditions. The gas-phase oxidation of toluene is well known to involve the formation of an oxygenated compound such as benzaldehyde.⁸ Use of benzaldehyde instead of toluene in the cross-coupling reaction ($C_6H_5CHO : O_2 : CH_4 = 0.75 : 4 : 50 \text{ cm}^3 \text{ min}^{-1}$ at NTP, with 1 g of the catalyst at 973 K) provided high benzaldehyde conversion (75%) giving the carbon oxides and benzene in 61 and 32% selectivities, respectively. These results suggest that even if the oxygenated compounds are generated, they are immediately subject to further oxidation into benzene and carbon oxides. This is consistent not only with the above experimental data but also with the absence of any oxygenated compounds in our reaction products.

In conclusion, toluene oxidative methylation using methane involves a cross-coupling between the methyl and benzyl radicals on the surface to form C_8 hydrocarbons; concurrent

methane-methane homo-coupling takes place in the gas phase.

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