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Alkylation of benzene with long chain (C8–C18) linear primary alcohols over zeolite-Y

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Linear alkyl benzenes (LAB) are important intermediates in the manufacture of detergents and surface active agents. The alkylation of benzene with linear alcohols using Y-type zeolite catalysts is described here. The alkylation of benzene with 1-decanol was carried out over RE-Na-Y, RE-HY, HY zeolite catalysts with high conversions of 1-decanol. All the positional isomers of phenyldecanes formed during the reaction were characterized by comparing the GC data with the authentic samples. The alkylation of benzene was also carried out using long chain linear alcohols (C8–C18) under similar reaction conditions and the isomer distribution in the product was studied.

Keywords: linear alkyl benzene, alkylation, phenyldecane, 1-decanol zeolite, RE-HY, HY, RE-Na-Y

1. Introduction

Long chain alkyl benzenes, especially linear alkyl benzenes (LAB), are very important intermediates in the manufacture of detergents and surfactants. The commercial alkyl benzenes are usually mixtures of C9–C14 linear alkyl side chain derivatives with the phenyl group attached to different C atoms in the chain [1]. It is believed that the 2-phenyl isomer gives detergent of better emulsibility and biodegradability [2]. These alkyl bezenes are prepared by Friedel–Crafts alkylation of benzene with long chain alkenes or alkyl halides using an acid catalyst [3,4]. The commercial process for LAB is based on alkylation of benzene with olefins using anhydrous HF as catalyst [1]. Due to the hazardous nature of HF, efforts have been made to replace it with environmentally safer catalysts. UOP has developed a solid acid [2] catalyst as a substitute for HF. Other solid acid catalysts reported for the alkylation of benzene with olefins include heteropolyacids [5], clays [6], ZSM-12 [7], HY [8], pillared clays [9] and $AlCl_3$ supported on silica [10]. We herein report our results on the alkylation of benzene with long chain (C8–C18) primary alcohols using zeolite catalysts and the isomer distribution of phenyl alkanes in the product. Although there are many reports on alkylation of benzene using zeolite catalysts with lower alcohols [11], the alkylation with long chain alcohols has not been studied. These long chain alcohols are readily accessible from natural sources such as palm kernel oil, coconut oil, tallow, etc.

2. Experimental

A commercial Na-Y catalyst (PQ Corporation, USA) was ion exchanged with rare earth (RE) chloride (obtained from Indian Rare Earth, Ltd., Udyogmandal, Kerala, India; 5 wt% solution; 10 ml/g of zeolite, 85 °C, duration = 5 h, 3 exchanges). The RE exchanged catalyst (RE-Na-Y) was filtered, washed free of chloride ions, dried at 90 °C and calcined at 450 °C. The ion exchange was found to be about 70%, ascertained by estimating the Na^+ ions in the filtrate. The HY catalyst was prepared by calcining NH_4-Y (obtained from PQ Corporation, USA, $SiO_2/Al_2O_3 = 4.6$) at 450 °C for 6 h. RE-HY was obtained from NH_4-Y by rare earth ion exchange following the same procedure as for RE-Na-Y and calcining the catalyst at 450 °C. H-mordenite ($SiO_2/Al_2O_3 = 17.7$) obtained from Norton, USA, was used. HZSM-5 ($SiO_2/Al_2O_3 = 40$), TS-1 ($SiO_2/Al_2O_3 = 80$) and H-β were obtained from Catalysis Division, National Chemical Laboratory, Pune, India. Linear chain primary alcohols (C8, C10, C12, C16 and C18) were obtained from Aldrich Chemical Co. (Milwaukee, WI). All five positional isomers of phenyldecane were synthesized independently by known sequence of reactions for the purpose of comparison.

The alkylation reaction was carried out with 1-decanol (5 g) and benzene (50 ml) in a Parr reactor of 300 ml capacity in the presence of zeolite (5 g) at 140 °C. The reaction mixture was analyzed by GC (column: BP-1, 25 m × 0.5 mm; programmed oven temperature: 100–180 °C, 2 min hold, 20 °C/min; carrier gas: helium, flow rate 6 ml/min; detector: FID, 300 °C; inj. port: 250 °C). The catalyst was freshly activated by calcining at 450 °C for 4 h before use. The product was isolated after removing the catalyst by filtration and distilling out the excess benzene.

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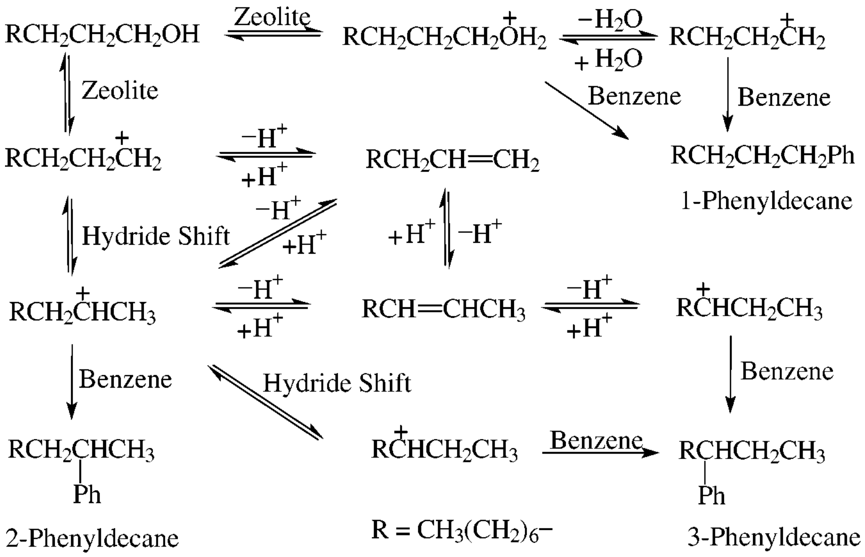
3. Results and discussion

Initially the alkylation of benzene with 1-decanol was carried out at benzene reflux temperature using rare earth exchanged Na-Y (RE-Na-Y). There was no alkyl benzene formation observed even after refluxing the reaction mixture for 24 h. However, the same reaction when carried out in a Parr reactor under autogeneous pressure at 140 °C for 6 h gave a quantitative conversion of decanol to a mixture of five isomeric phenyldecanes. The formation of these isomeric linear phenyldecanes and their order of elution in GC was established by comparing their retention times with the retention times of the individual authentic samples of isomeric linear phenyldecanes synthesized by known sequence of reactions. The order of elution with increasing retention time is as 5-, 4-, 3-, 2- and 1-phenyldecane.

1-phenyldecane may arise either by the reaction of a primary carbocation formed during the reaction with benzene or direct alkylation of benzene with 1-decanol in the presence of a zeolite catalyst. The primary carbocation can isomerize to the more stable secondary carbocation by a hydride shift or it can loose a proton to give an olefin. This terminal olefin can isomerize to other olefins by hydrogen transfer, which after reacting with benzene can give all five positional isomers (scheme 1). The super cavity in the Y-zeolite (cage diameter 1.30 nm) is large enough to accommodate the transition state for the alkylation products.

There is yet another possibility of isomerization of initially formed alkylbenzene itself under the reaction conditions to other positional isomers. To rule out this possibility, a mixture of 1-phenyldecane, benzene and the RE-Na-Y catalyst was heated in a Parr reactor at 140 °C for 6 h and the reaction mixture was analyzed by GC. The GC analysis of this reaction mixture showed the presence of only unchanged 1-phenyldecane and did not show even a trace of 2-, 3-, 4- or 5-phenyldecane. However, when pure 2-phenyldecane was heated in a Parr reactor under similar reaction conditions it gave an equilibrium mixture of unchanged 2-phenyldecane (90%) and the other four positional isomers (total 10%). This suggests that the rate of isomerization of 2-phenyldecane is much slower than the isomerization of the carbocation or olefin.

To optimize the reaction time, the alkylation of benzene with 1-decanol was carried out in a Parr reactor at 140 °C using RE-Na-Y and samples were drawn at regular intervals of time and analyzed by GC. The conversion of 1-decanol and the distribution of positional isomers in the product are summarized in table 1. The alkylation is almost complete within 5 h (figure 1) and the composition of isomers in the product remains almost the same (figure 2) with higher selectivity for 2-phenyldecane. The position of the phenyl



Scheme 1. Possible mechanism for the formation of positional isomers of phenyldecane.

Table 1
Alkylation product of benzene with 1-decanol at 140 °C using RE-Na-Y catalyst.

Time[a] (h)	Conversion of 1-decanol (%)	Selectivity for positional isomers of phenyldecanes (%) 1-Ph	2-Ph	3-Ph	4-Ph	5-Ph
1	35.0	15.5	30.0	20.4	15.5	18.6
2	87.6	11.2	33.2	21.8	16.5	17.3
3	88.0	11.2	32.9	21.8	17.0	17.1
4	95.0	10.8	32.9	21.8	17.2	17.3
5	98.0	9.4	33.0	22.4	17.5	17.7

[a] Time intervals at which samples were drawn and analyzed by GC.

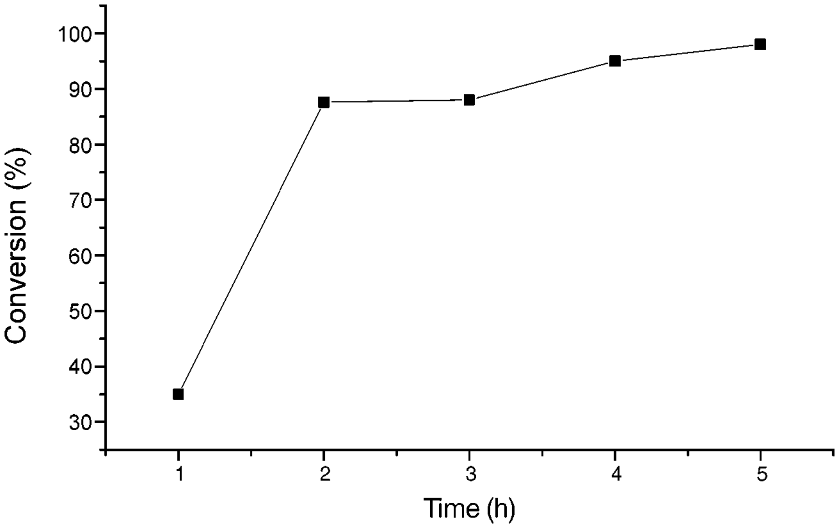


Figure 1. Conversion of 1-decanol to phenyldecane with respect to time.

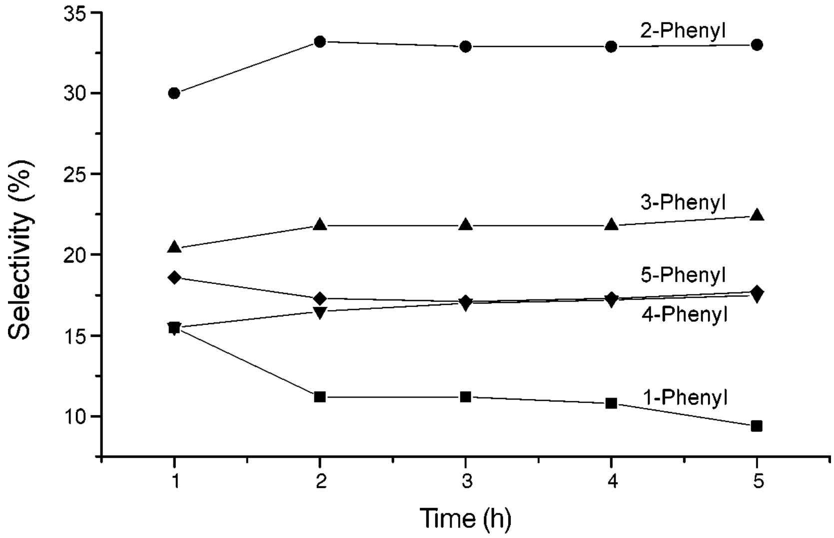


Figure 2. Selectivity for the isomers of phenyldecane at various time intervals.

group on the alkyl chain and the alkyl chain length are important factors in the determination of biodegradability and surface active properties, when sulfonates are prepared from LAB. Best results are obtained with an alkyl chain length in the range of 9–14 carbon atoms and higher 2-phenyl isomer content. Sivasankar and Thangaraj [12] have done a comparative study of alkylation of benzene with 1-dodecene and the distribution of isomers in the product. They showed that the percentage of 2-phenyl is higher with a zeolite catalyst than with H_2SO_4, HF or $AlCl_3$. We have also observed formation of phenyldecanes with higher 2-phenyl content in the alkylation of benzene with 1-decanol using a zeolite catalyst.

Various other zeolite catalysts were screened for this alkylation reaction of benzene with 1-decanol (table 2). Amongst the various catalysts tried for alkylation, the selectivity towards LAB was very high in case of the Y-type zeolite catalyst (RE-Na-Y, RE-HY and HY). Although zeolite H-β showed high selectivity for 2-phenyl isomer, the number branched alkylated products (total 15%) were also formed along with other linear alkylbenzenes. H-ZSM-5, TS-1 and H-mordenite catalysts were found unsuitable for the alkylation reaction [13]. The low performance of these catalysts towards alkylation may be attributed to the lack of large enough void space, which restricts the formation of transition state for alkylation reaction.

Based on the performance of the catalyst with respect to the conversion and the production of linear alkylbenzene, the RE-Na-Y catalyst was selected for the alkylation of benzene with other linear alcohols having 8–18 carbon chain. The yields of alkylated products and their isomer distribution are summarized in table 3. It is clear that a wide variety of alcohols can be used for the alkylation of benzene using RE-Na-Y. The formation of 5-phenylalkane in case of C10 and C12 alcohols and 6-phenylalkane in case of C16 and C18 alcohols was observed, as the rate of re-

Table 2
Alkylation of benzene with 1-decanol using different catalysts.[a]

Catalyst	Conversion of 1-decanol (%)	Selectivities for positional isomers of phenyldecanes[b] (%)					
		1-Ph	2-Ph	3-Ph	4-Ph	5-Ph	Others
RE-Na-Y	100	9.4	33.0	22.4	17.5	17.7	–
RE-HY	100	12.3	29.7	22.4	17.7	17.9	–
H-Y	100	8.9	29.9	23.5	18.6	19.1	–
H-β	100	4.6	42.6	24.0	11.1	2.4	15.3
H-mordenite		No alkylation products					
H-ZSM-5		No alkylation products					
TS-1		No alkylation products					

[a] The reactions were carried out in a Parr reactor using catalyst : 1-decanol : benzene (1 : 1 : 5, w/w/v) at 140 °C under autogeneous pressure for 6 h.
[b] GC analysis.

Table 3
Alkylation of benzene with different alcohols using RE-Na-Y catalyst at 140 °C.

Alcohol	Yield[a] (%)	Isomer distribution of phenylalkanes[b] (%)					
		1-Ph	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph
C8	88	7.65	31.40	28.73	32.22	–	–
C10	95	11.02	30.18	21.52	17.62	19.66	–
C12	96	8.26	21.67	19.66	17.96	32.45	trace
C16	94	11.61	19.32	14.89	12.09	11.14	30.95
C18	97	9.52	18.92	14.39	11.52	10.73	34.92

[a] Isolated yields.
[b] Area % by GC.

arrangement of carbonium ion is faster than the alkylation of benzene [14]. However, 7-phenyl and higher isomers were not formed in detectable amounts.

4. Conclusion

The alkylation of benzene with 1-decanol using Y-zeolite catalysts gave very high conversion of linear alkyl benzenes. The isomer distribution in the alkylated product showed high content of 2-phenyldecane, which is essential for good detergent properties. The RE-Na-Y catalyst was found to be very effective in the alkylation of benzene with other long chain linear alcohols having 8–18 carbons.

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