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Reactive distillation for sustainable, high 2-phenyl LAB production

John F. Knifton[a,*], Prakasa Rao Anantaneni[b], P. Eugene Dai[✠], Melvin E. Stockton[b]

[a] Shell Global Solutions, Houston, TX 77251, USA
[b] Huntsman Corporation, Austin, TX 78761, USA

Abstract

Linear alkylbenzenes (LABs) comprising >80% 2-phenyl isomer content, have been prepared in sustainable high yields from detergent-range linear olefins via regioselective benzene alkylation using reactive distillation technology. Hydrofluoric acid (HF)-treated mordenites provide enhanced, shape-selective, alkylation performance when employed as heterogeneous catalysts in the subject syntheses. Both individual C_{10}–C_{12} α-olefins, as well as mixed, commercial plant-derived, C_{10}–C_{14} paraffin dehydrogenate feedstocks containing ca. 8.5% internal olefins, have been successfully alkylated for extended periods using the reactive distillation mode of operation.

Keywords: Reactive distillation; Linear alkylbenzenes; Regioselective alkylation; Fluorided mordenite

1. Introduction

US production of linear alkylbenzenes (LABs) currently exceeds 1 billion lb per year [1] and global consumption is predicted to grow at an annual rate of 3.6%. The practice of this chemistry on a commercial scale can still, however, present peculiar challenges, particularly regarding:

- the regioselectivity of the alkylation is difficult to control;
- there is a significant increase in market demand for the 2-phenyl isomers;
- polyalkylaromatic and tetralin by-product formation must be strictly limited;
- accumulation of an aqueous component in the reactor system is detrimental.

Traditionally, the production of linear alkylbenzenes from detergent-range olefins plus benzene has been practiced commercially using either Lewis acid catalysts, or liquid hydrofluoric acid (HF) [2]. The HF catalysis typically gives 2-phenylalkane selectivities of only 17–18%. More recently, UOP/CEPSA have announced the Detal® process for LAB production that is reported to employ a solid acid catalyst [3]. Within the same time frame, a number of papers and patents have been published describing LAB synthesis using a range of solid acid (sterically constrained) catalysts, including acidic clays [4], sulfated oxides [5], plus a variety of acidic zeolite structures [6–9]. Many of these solid acids provide improved 2-phenylalkane selectivities.

We have demonstrated that linear alkylbenzenes comprising >80% 2-phenyl isomer content, can be prepared in sustainable high yields from detergent-range

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[*] Corresponding author. Tel.: +1-281-544-6917; fax: +1-281-544-7512.
E-mail address: john.knifton@shell.com (J.F. Knifton).

[✠] Deceased.

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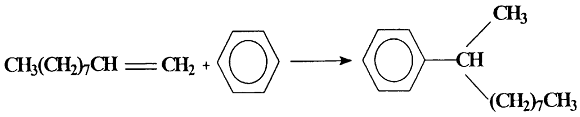
linear α-olefins via stereo-selective benzene alkylation using reactive distillation technology in combination with HF-treated mordenite catalysis. The acid-modified mordenite catalysts provide enhanced stereo-selective alkylation performance when employed as heterogeneous catalysts in the subject syntheses. Both individual C_{10}–C_{12} α-olefin cuts, as well as mixed, commercial plant-derived, C_{10}–C_{14} paraffin dehydrogenate feedstocks containing ca. 8.5% internal olefins, have been successfully alkylated. Stereo-selective alkylation of 1-decene to 2-phenyldecane is illustrated by Eq. (1).



(1)

Catalyst lives exceeding 3000 h on stream have been demonstrated with the fluorided mordenite catalysts using reactive distillation technology. When feeding typical C_{10}–C_{14} paraffin dehydrogenate, average C_{10}–C_{14} olefin conversions are near quantitative, while 2-phenyl LAB selectivities are in the range 74–84%. The bromine numbers of these LAB products are typically <0.5, with only trace formation of undesirable dialkylated benzene homologues and tetralin derivatives. The reactive distillation mode ensures that the catalyst bed is continuously washed of any heavy organics, thereby extending the catalyst life. Additional improvements in catalyst performance are realized by continuous removal of any aqueous fraction from the catalyst area.

The fluoride-treated acidic mordenite catalysts have, in fact, the triple advantages of:

1. high alkylation activity that allows quantitative alkene conversions at adequate feed rates;
2. exceptionally high regioselectivity for the more desirable 2-phenyl LAB;
3. sustainable alkylation activity that ensures long catalyst life, ease of handling, and ready regeneration.

2. Experimental

The mordenite zeolites used in this study were purchased from both PQ Corporation (CBV-20A, silica/alumina molar ratio 20, Na_2O content 0.02 wt.%, surface area 550 m^2/g, in ca. 1.5 mm extruded form) and from Union Carbide Corporation (LZM-8, silica/alumina molar ratio 17, Na_2O content 0.02 wt.%, surface area 517 m^2/g in powder form). All samples were calcined at 540 °C prior to use.

The following example illustrates the preparation of a hydrogen fluoride-modified mordenite. To a 500 g sample of acidic, dealuminized mordenite (CBV-20A from PQ Corporation, 1.5 mm diameter extrudates that had been calcined at 538 °C, overnight) was added a solution of 33 ml of 48% HF in 1633 ml of distilled water, and the mix cooled in ice, stirred on a rotary evaporator overnight, then filtered to recover the extruded solids. The extrudates were further washed with distilled water, dried in vacuo at 100 °C, and then calcined at 538 °C, overnight. Analyses of the treated mordenite showed: 1.2% fluoride, 0.49 meq./g acidity. Samples were charged to the reactive distillation unit either as 20/40 mesh granules, or as ca. 1.5 mm extrudates.

Individual α-olefin feedstocks were purchased from Aldrich. The C_{10}–C_{14} paraffin dehydrogenate was obtained from a commercial LAB plant and contained 8.5% C_{10}–C_{14} olefins, primarily a mixture of internal olefins.

Continuous benzene alkylation was conducted in a reactive distillation column of the type illustrated in Fig. 1. The process unit comprises the following principal elements: a double column of solid catalyst 32, packing columns above and below the catalyst bed, a liquid reboiler 42 fitted with a liquid bottoms product takeoff 44, a condenser 21 fitted with a water collection and takeoff, and a feed inlet 14 above the catalyst column, plus the necessary temperature and pressure controls. The feed mixture of benzene and olefin flows from a feed pump 10 to a feed inlet 14 via line 12 and falls to the packed acidic catalyst bed 32 where alkylation takes place. Typically, the catalyst bed comprises two parts, one 24 cm in length, the other ca. 55 cm and has a total volume of about 250 cm^3. In the catalyst bed 32, the falling feed also contacts rising vapors of unreacted benzene which have been heated to reflux in reboiler 42 by heater 40. Such rising vapors pass over the thermocouples 28 and 38, which monitor temperature and provide feedback to heater 40. The rising vapors also pass through standard, woven-mesh, stainless-steel, Goodloe packing 36 that holds the catalyst beds in place. A small plug of glass wool/Goodloe

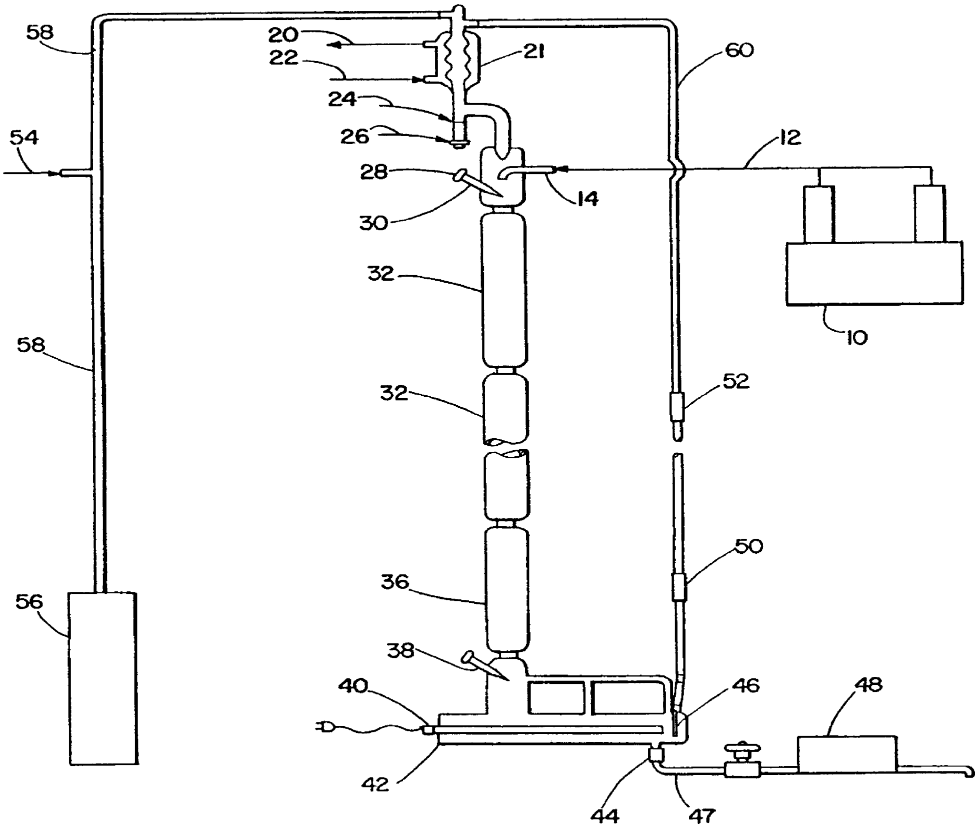


Fig. 1. Schematic of reactive distillation unit used for LAB synthesis.

packing above the catalyst bed 32 prevents the smaller particles from reaching the feed inlet 14.

Prior to start-up, the reboiler is charged with 100–500 ml of benzene/olefin feed mix, and the complete system is flushed with nitrogen, which enters via line 54. Also, prior to start-up, it may be desirable to heat the catalyst bed so as to remove any residual moisture. Trace moisture in the feed mix is collected in water trap 24 after liquifying at condenser 21. The reboiler mix is then heated to reflux and the benzene/olefin mix continuously introduced into the unit above the catalyst bed as described above. When the LAB content in the reboiler 42 rises to the desired level, the bottoms LAB product is removed from the system via line 47 and valve 44. The dip tube 46 is employed to slightly increase the pressure in the reboiler 42. Alternatively, a pressure generator 56 may be employed. Control mechanisms for heat shut-off 50 and pump shut-off 52 serve to close down heat/feed if the liquid level in the system rises too high. Line 60 connects the pump shut-off 52 to the system above the condenser 21. With typical benzene/olefin feed rates of 50–500 ml/h, and benzene-to-olefin feed molar ratios in the range 5:1–40:1, the temperature profile in the two-part catalyst beds 32 is generally within the range of 80–120 °C, according to the applied unit pressure. The reboiler temperature is maintained, for the most part, below 150 °C [10].

3. Results and discussion

Aromatic alkylation is illustrated in this paper for both individual α-olefin cuts (e.g. 1-decene and 1-dodecene) as well as typical samples of C_{10}–C_{14} paraffin dehydrogenate that contain ca. 8.5% C_{10}–C_{14}

olefins, primarily internal olefins. Syntheses have, for the most part, been conducted in a continuous reactive distillation unit of the type illustrated in Fig. 1, operated slightly above atmospheric pressure. Operational details for this unit may be found in the previous section.

As part of our studies into the use of solid acid catalysis for LAB production, we have screened the performances of at least four potential candidates, including fluorided montmorillonite clays, zeolite beta, dealuminized mordenite, and fluorided, dealuminized mordenites [10–12]. The fluorided mordenite catalysts generally provided the highest regioselectivity for a variety of olefin feedstocks [13]. Their preparation is detailed in Section 2. The dealuminized, mordenite precursors typically have silica/alumina ratios in the range 10:1–50:1, plus low sodium contents, and after HF treatment, their fluoride contents are generally in the range 0.1–4%. The HF treatment is likely to decrease the total Bronsted acid site density, but increase the strength of the remaining acid sites in the mordenite. This, in turn, would be expected to raise the reactivity of the carbocation intermediates formed during LAB synthesis. Surface fluorination of H-mordenite has been reported previously to increase the catalyst alkylation activity and enhance the stability [14].

Under batch, refluxing benzene conditions (ca. 80 °C), where the starting benzene/1-dodecene molar ratio is ca. 25 [10], we observe:

- dodecene conversions are close to quantitative after 3 h;
- 2-phenyldodecane isomer selectivity is 79.9%;
- heavies constitute only ca. 0.2%.

A detailed analysis of the LAB isomer distribution in this experiment is provided in Table 1. The results are very similar for LAB production from benzene/1-decene mixtures using the same batch procedures and equipment (see also Table 1).

The fluorided mordenite catalysts are particularly effective for benzene alkylation with typical, plant-derived, C_{10}–C_{14} paraffin dehydrogenate. Fig. 2 illustrates continuous alkylation over 250 h using a 1.2% fluorided mordenite catalyst (250 cm^3) in the reactive distillation unit of Fig. 1. Feeding a benzene/paraffin dehydrogenate mix (10:1 molar C_6H_6/C_{10}–C_{14} olefin) the 2-phenyl isomer selectivity remains in the range 75–83%, while total olefin conversions are above 95%. The recovered HF-treated mordenite shows <10% loss of fluoride and a maintained acidity (1.1% F, 0.29 meq./g titratable acidity). One of the intrinsic advantages of the reactive distillation configuration (Fig. 1), is that the rising benzene vapors from the reboiler continually wash the HF/mordenite catalyst of heavy organics, thereby increasing the lifetime of the solid acid. Improved catalyst life and performance is further enhanced through continuously removing any water fraction from the catalyst area. By better mixing of C_{10}–C_{14} olefin and benzene reactants and increasing the instantaneous C_6H_6 concentration in the alkylation zone, we are able to achieve selective benzene monoalkylation, with only trace quantities of undesirable dialkylated benzene homologues and tetralin derivatives (see Tables 1 and 2).

Table 1
Benzene alkylation with 1-dodecene and 1-decene, using fluorided mordenite catalyst

	Dodecene conversion (99.7%)	Decene conversion (99%)
LAB isomer distribution (%)		
2-Ph	79.9	84
3-Ph	16.6	13
4-Ph	0.8	2
5-Ph	1.3	1
6-Ph	1.3	
Heavies (%)	0.2	
Linear LAB (LLAB)	95.9	

Fig. 2 also includes a comparative experiment, where the solid acid catalyst is a sample of non-fluorided (but calcined), acidic mordenite. Here we see: (a) a significant loss of alkylation activity with time on stream; and (b) a measurably lower 2-phenyl isomer content. The 2-phenyl isomer selectivity (70–75%) observed in this second experimental series is, however, within the range reported earlier by Travers et al., who also used non-fluorinated, but dealuminized, mordenite catalysts for benzene/1-dodecene batch alkylation [6].

Performances of these acidic mordenite zeolites have been examined as a function of the level of fluoride treatment. For mordenites treated with HF to fluoride levels of 0.25, 0.5, and 1.0%, batch alkylation

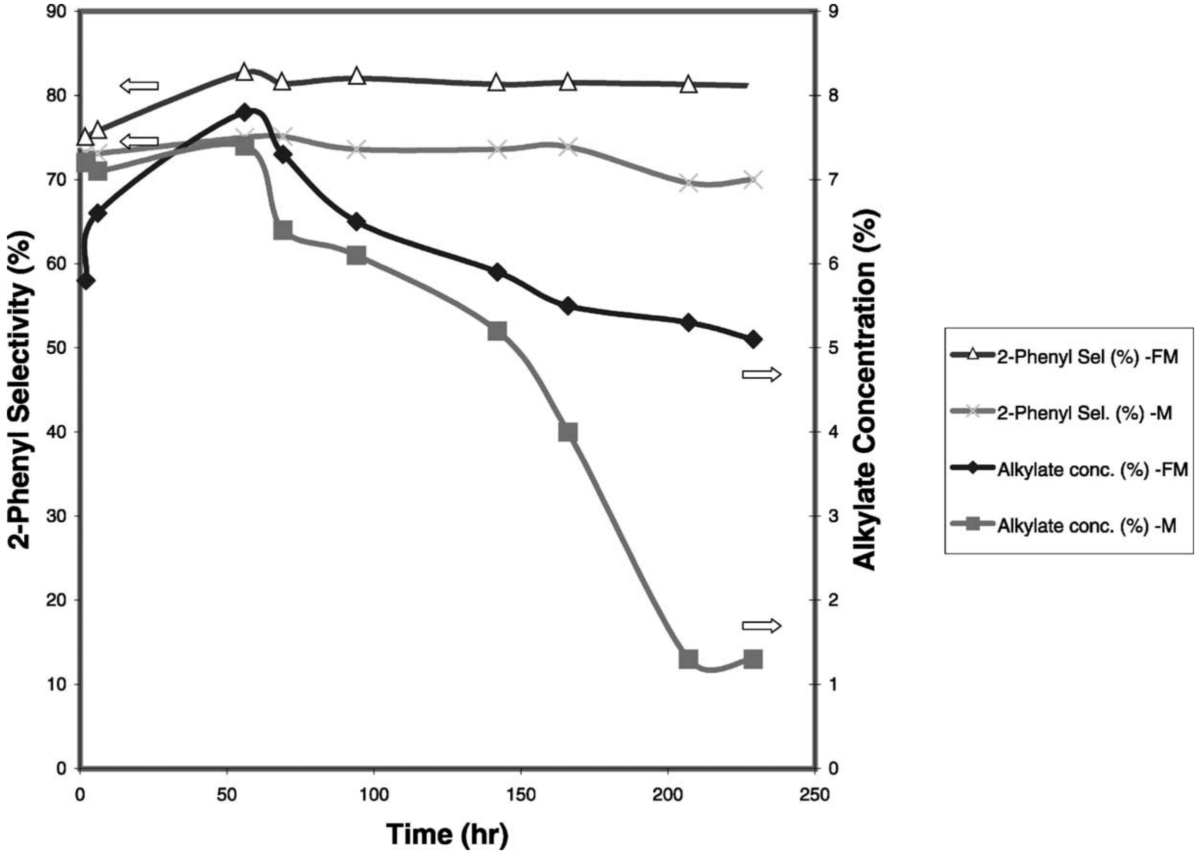


Fig. 2. Benzene alkylation with C_{10}–C_{14} paraffin dehydrogenate: FM, using fluorinated mordenite catalyst; M, using the non-fluorinated mordenite precursor.

at ca. 80 °C of typical benzene/1-dodecene mixtures show (after 1 h) very similar levels of activity and 2-phenyl selectivity (see Table 2). A more heavily loaded, 4.8% fluorided mordenite (catalyst D), however, was inactive. Analyses of the freshly-treated mordenites by MAS NMR indicated that the mildly-treated catalysts A–C still retained their tetrahedral Al, whereas there was no framework tetrahedral Al remaining in the case of catalyst D and the sample was completely dealuminized [15]. Soled et al. report that severe fluoridation also leads to the conversion of non-framework aluminum species to AlF_3 [16].

Catalyst lives well in excess of 3000 h on stream have been demonstrated with the fluorided mordenite

Table 2
Benzene alkylation with 1-dodecene, fluorided mordenite catalysts

Catalyst	Fluoride level (%)	Dodecene conversion (%)	LAB isomer distribution (%)					Heavies (%)
			2-Ph	3-Ph	4-Ph	5-Ph	6-Ph	
A	0.25	>90	71.6	22.9	2.9	1.1	1.3	0
B	0.5	>90	73	22.2	2.9	1.2	0.8	0
C	1	>90	74.3	19.5	2.9	3.4		0
D	4.8	<1						

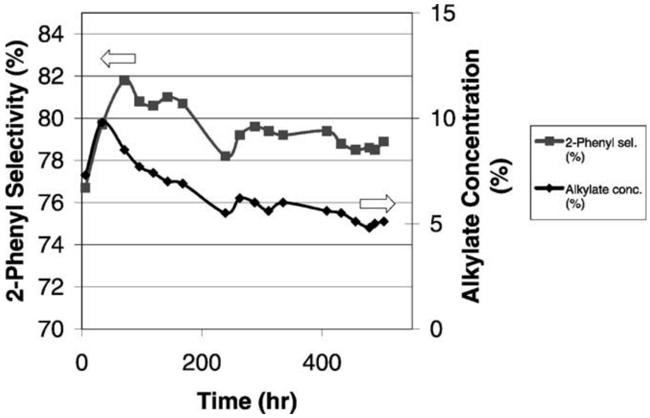


Fig. 3. Benzene alkylation with C_{10}–C_{14} paraffin dehydrogenate catalyzed by fluorinated mordenite.

catalysts using the reactive distillation technology. When feeding typical C_{10}–C_{14} paraffin dehydrogenate at LHSV of 0.2, average C_{10}–C_{14} olefin conversions are near quantitative, while 2-phenyl LAB selectivities are in the range 74–84%. The bromine numbers of these stripped LAB products are typically 0.1 → 0.5. Illustrative data may be found in Fig. 3. Elemental analyses of the recovered catalyst in this case shows 1.0% fluoride and a titratable acidity of 0.34 meq./g. MAS NMR studies indicate some loss of tetrahedral alumina [15]. Generally, for typical used HF/mordenite samples, carbon is fairly evenly distributed throughout the sample. For partially deactivated catalysts, the deposits are mainly polyalkylated aromatics. Polymer coke is prevalent in fully deactivated samples. Nevertheless, a simple calcination will fully restore alkylation activity and sustainable life-times in C_{12}–C_{14} paraffin dehydrogenate/benzene service of >3000 h have been demonstrated.

References

[1] Chemical Economics Handbook, Stanford Research Institute International, 1999.
[2] Encyclopedia of Chemical Technology, vol. 2, Wiley, New York, p. 58.
[3] T. Imai, J.A. Kocal, B.V. Vora, Sci. Technol. Catal. (1994) 339.
[4] H. Ming-Yuan, L. Zhonghui, M. Enze, Catal. Today 2 (1988) 321.
[5] J.H. Clark, G.L. Monks, D.J. Nightinggale, P.M. Price, J.F. White, J. Catal. 193 (2000) 348.
[6] C. Travers, F. Raatz, B. Juguin, G. Martino, Eur. Patent 466558 (1992), to Institute Francais du Petrol.
[7] Y. Cao, R. Kessas, C. Naccache, Y.B. Taarit, Appl. Catal. 184 (1999) 231.
[8] Z. Da, P. Magnoux, M. Guisnet, Catal. Lett. 61 (1999) 203.
[9] L.B. Young, US Patent 4,301,317 (1981), to Mobil Oil Corp.
[10] J.F. Knifton, P.R. Anantaneni, M. Stockton, 5,770,782 (1998), to Huntsman Petrochemical Corp.
[11] J.F. Knifton, P.R. Anantaneni, 5,777,187 (1998), to Huntsman Petrochemical Corp.
[12] J.F. Knifton, P.R. Anantaneni, P.E. Dai, 5,847,254 (1998), to Huntsman Petrochemical Corp.
[13] J.F. Knifton, P.R. Anantaneni, P.E. Dai, M.E. Stockton, Catal. Lett. 75 (2001) 113.
[14] A. Kurosaki, S. Okazali, Bull. Chem. Soc. Jpn. 63 (1990) 2367.
[15] J.F. Knifton, J.C. Edwards, unpublished results.
[16] S. Soled, G.B. McVicker, J.J. Ziemiak, G. DeMartin, L. Yacullo, K. Strohmaier, J. Miller, in: Proceedings of the 206th American Chemical Society Meeting, Division of Petroleum Chemistry, Chicago, 1993, p. 546 (Preprints).