A new, improved, solid-acid catalyzed process for generating linear alkylbenzenes (LABs)

John F. Knifton*, Prakasa Rao Anantaneni, P. Eugene Dai and Melvin E. Stockton
Huntsman Corporation, Austin, TX 78752, USA

Received 2 May 2001; accepted 31 May 2001

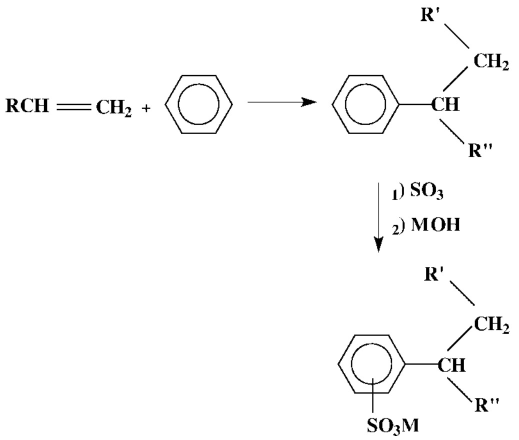
Linear alkylbenzenes (LABs) comprising >80% 2-phenyl isomer content, have been prepared in high yields from detergent-range linear olefins *via* regioselective benzene alkylation. HF-treated mordenites, acidic Beta-zeolites, and fluorided montmorillonite clays, each provide enhanced shape-selective alkylation performance when employed as heterogeneous catalysts in the subject syntheses. Both individual C_8–C_{12} α-olefins, as well as mixed, commercial plant-derived, C_{10} through C_{14} paraffin dehydrogenate feedstocks containing *ca.* 8.5% internal olefins, have been successfully alkylated for extended periods using reactive distillation technology.

KEY WORDS: linear alkylbenzenes; regioselective alkylation; fluorided mordenite; reactive distillation

1. Introduction

The carbonium ion alkylation of arenes with detergent-range, linear olefins, catalyzed by protonic acids typically produces linear, secondary phenylalkanes (LABs) that are a mix of positional isomers (equation (1)), *i.e.*, 2-phenyl, 3-phenyl, *etc.* [1]. US production of LAB currently exceeds one billion lb/yr [2], 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, specifically where, in the case of benzene alkylation, there is now an increasing need to preferentially generate the more desirable 2-phenyl alkylate (where in equation (1), R'' is methyl), and to avoid the formation of non-linear alkylbenzenes. The 2-phenyl isomers are preferred because, amongst the possible phenylalkane sulfonate (LAS) isomer derivatives (equation (2)), the 2-phenyl LAS ($R'' = CH_3$) have the most favorable biodegradation and solubility characteristics [3].
- The use of long-chain alkenes may result in the formation of significant quantities of heavy organics – particularly polyalkylaromatics and tetralin derivatives, together with carbonaceous deposits.
- The low mutual solubilities of the liquid alkenes with the liquid aromatics may necessitate alternative mixing procedures in order to achieve high yields of desired products.
- The low temperatures needed to conduct this alkylation selectively may result in the accumulation of water in the reactor, brought in with the alkylation feed components.



(1)

(2)

where $R'' + R' = R$, R'' is CH_3 or a homologue, and $M = Na$, $Mg_{1/2}$, $Ca_{1/2}$, or $Ba_{1/2}$.

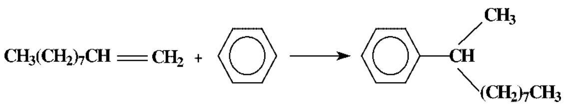
Traditionally, the production of linear alkylbenzenes (LABs) from detergent range olefins plus benzene has been practiced commercially using either Lewis acid catalysts, or liquid hydrofluoric acid (HF) [1]. The HF catalysis typically gives 2-phenylalkane selectivities of only 17–18%. More recently, UOP/CEPSA have announced the Detal^R process for LAB production that is reported to employ a solid acid catalyst [4]. 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 [5], sulfated oxides [6], plus a variety of acidic zeolite structures [7–10]. Many of these solid acids provide improved 2-phenylalkane selectivities.

We have discovered that linear alkylbenzenes with >80% 2-phenyl content can be generated using fluoride-treated acidic mordenite catalysts and that benzene alkylation with a variety of olefin feed-stocks can be maintained with these HF/mordenite catalysts for extended periods through

---

* Present address: Shell Chemical Company, PO Box 1380, Houston, TX 77251-1380, USA.

the use of reactive distillation techniques [11–13]. This chemistry is illustrated in equation (3) for the synthesis of 2-phenyldecane.



(3)

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 1/16″ extruded form) and from Union Carbide Corporation (LZM-8, silica/alumina molar ratio 17, Na_2O content 0.02%, 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, SiO_2/Al_2O_3 molar ratio 20, Na_2O, 0.02 wt%, surface area 550 m^2/g, 1/16″ 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 of Beta zeolite, comprising 80% β-zeolite (SiO_2/Al_2O_3 molar ratio 23.9) and 20% alumina binder, in 1/16″ diameter extruded form, were purchased from PQ Corporation.

The preparation of hydrogen fluoride-modified montmorillonite clays has been described by us previously [14]. All untreated clay samples were purchased from Engelhard Corporation.

Individual α-olefin feedstocks were purchased from Aldrich Chemical Company. 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 of the type illustrated in figure 1. The process unit comprises the following principal elements: a 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

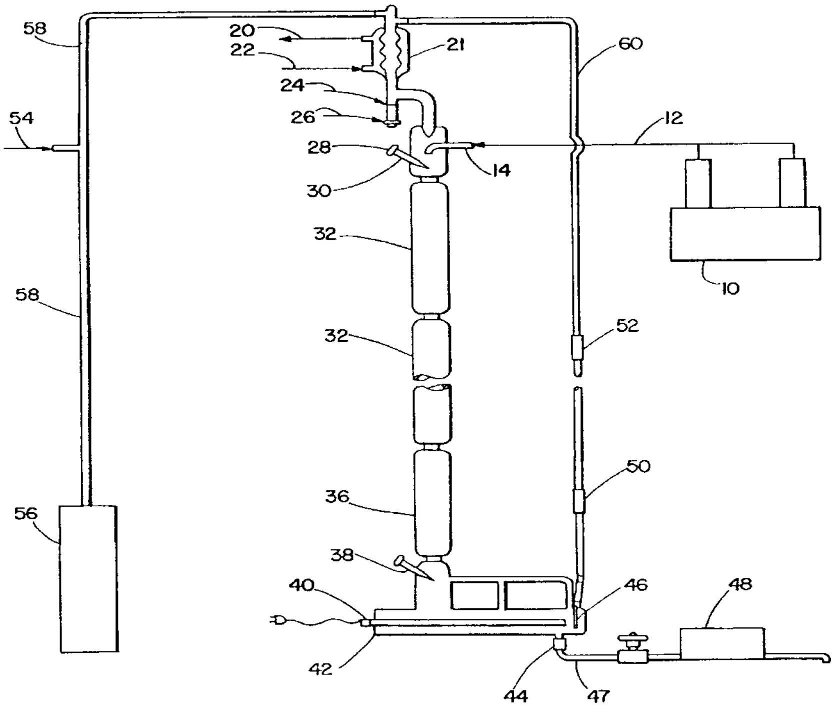


Figure 1. Schematic of reactive distillation unit used for LAB synthesis.

Table 1
Benzene/α-olefin alkylation with fluorided clay and Beta zeolite catalysts.

Ex.	Catalyst	Alkene	Benzene/alkene molar ratio	Benzene/alkene feed rate (LHSV) (h^{-1})	Catalyst bed diameter (cm)	Alkene conv. (%)	2-phenyl sel. (%)
1	F-clay	1-decene	20	0.08	2.5	98	38
2	F-clay	1-decene	20	0.4	2.5	>99	38
3	F-clay	1-decene	20	1	4.1	50	38
4	F-clay	1-decene	10	0.4	4.1	99	36
5	F-clay	1-decene	5	0.4	4.1	96	35
6	F-clay	1-octene	10	0.4	4.1	99	40
7	Beta zeolite	1-decene	20	0.08	4.1	>95	50
8	Beta zeolite	1-decene	20	0.4	4.1	62	47

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 thermocouple **38**, which monitors temperature and provides 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.

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**.

3. Results and discussion

Four classes of solid acid catalyst have in fact been considered in this work for benzene alkylation. They are:

- fluorided montmorillonite clays;
- zeolite Beta;
- dealuminized mordenite;
- fluorided, dealuminized mordenites.

Alkylation has been studied using 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 contains *ca.* 8.5% C_{10}–C_{14} olefins, primarily internal olefins. Syntheses were, for the most part, conducted in a continuous reactive distillation unit of the type illustrated in figure 1, operated slightly above atmospheric pressure. Operational details for this unit may be found in the experimental section.

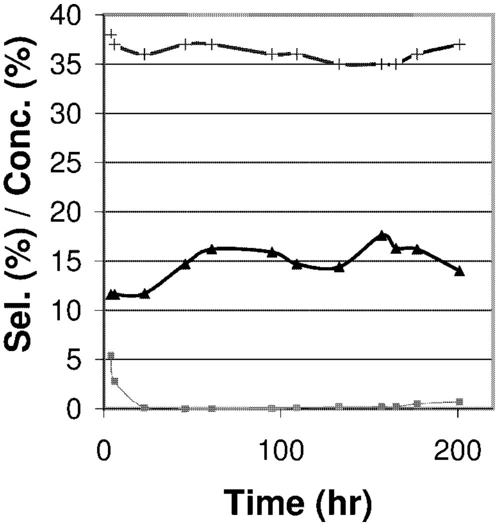


Figure 2. Benzene alkylation with 1-decene, using 0.5% HF on acidic montmorillonite clay catalyst. (▲) Total Ph-C_{10} conc. (%), (■) total decene conc. (%), and (+) 2-Ph-C_{10} selectivity (%).

Benzene alkylation with 1-decene using the acidic montmorillonite clays was examined over a range of experimental conditions. A 0.5% HF on acidic montmorillonite clay, dried *in vacuo*, and ground to 20/60 mesh [14] was employed. Typically feeding excess benzene (benzene/1-decene molar ratio 20/1), the 2-phenyldecane isomer selectivity (equation (3)) was *ca.* 38% at olefin conversions >90%, see table 1, ex. 1. Performance of these fluorided clays has been examined as a function of the benzene/1-decene feed composition, total liquid feed rate (liquid hourly space velocity, LHSV), and operating configuration (table 1). Switching to 1-octene as the co-feed, the 2-phenyl-C_8 selectivity rose to 40% (ex. 6). Extended runs with the same 0.5% HF/clay catalyst, but feeding benzene/1-decene (10/1 molar) led to very little change in alkylation activity, or 2-phenyldecane isomer selectivity, over a 200 h run period, see figure 2. During the majority of this experiment, it was observed that:

- decene conversions were quantitative;
- 2-phenyldecane isomer distribution was 35–38%.

Table 2
Benzene alkylation with 1-dodecene, fluorided mordenite catalyst.

Dodecene conv.	LAB isomer distribution (%)					Heavies	Linear LAB
(%)	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph	(%)	(LLAB)
99.7	79.9	16.6	0.8	1.3	1.3	0.2	95.9

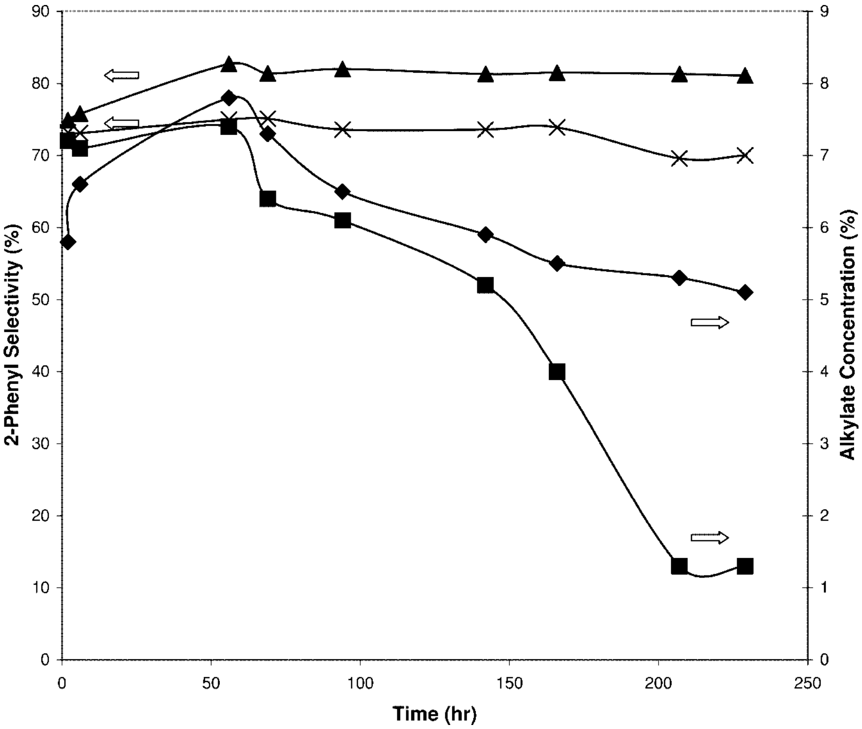


Figure 3. Benzene alkylation with C_{10}–C_{14} paraffin dehydrogenate; FM – using fluorinated mordenite catalyst; M – using the non-fluorinated mordenite precursor. (▲) 2-phenyl selectivity (%) FM, (×) 2-phenyl selectivity (%) M, (◆) alkylate concentration (%) FM, and (■) alkylate concentration (%) M.

Higher 2-phenyl-C_{10} selectivities were realized when switching to Beta-zeolite (silica/alumina 23.9) as the solid acid catalyst. Under steady state conditions, the 2-phenyldecane isomer content was now *ca.* 50%, at near quantitative decene conversion levels, see table 1, ex. 7–8. These data are consistent with the earlier batch studies by Young [10] for a range of large-pore zeolites, including β-zeolite.

A further, and substantial improvement in 2-phenyl isomer selectivity was achieved by using a HF-treated mordenite catalyst, prepared as described in section 2. These acidic, dealuminized, mordenite zeolite catalysts typically have silica/alumina ratios in the range 10 : 1 to 50 : 1, plus low sodium contents, and after HF treatment, their fluoride contents are generally in the range 0.1 to 4%. The HF treatment is likely to decrease the total Brønsted 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 both the catalyst alkylation activity, as well as enhancing the stability [15]. Under batch, refluxing benzene conditions (*ca.* 80 °C), we have observed:

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

The detailed distribution of LAB isomers in this experiment is provided in table 2.

The fluorided mordenite catalysts are particularly effective for benzene alkylation with typical, plant-derived, C_{10}–C_{14} paraffin dehydrogenate. Figure 3 illustrates continuous alkylation over 250 h using a 1.2% fluorided mordenite catalyst (250 cm^3) in the reactive distillation unit of figure 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, illustrated here in figure 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 instan-

Table 3
Benzene alkylation with 1-dodecene, fluorinated mordenite catalysts.

Catalyst	Fluoride level (%)	Dodecene conv. (%)	LAB isomer distribution 2-Ph	3-Ph	4-Ph	5-Ph	6-Ph	Heavies (%)
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						

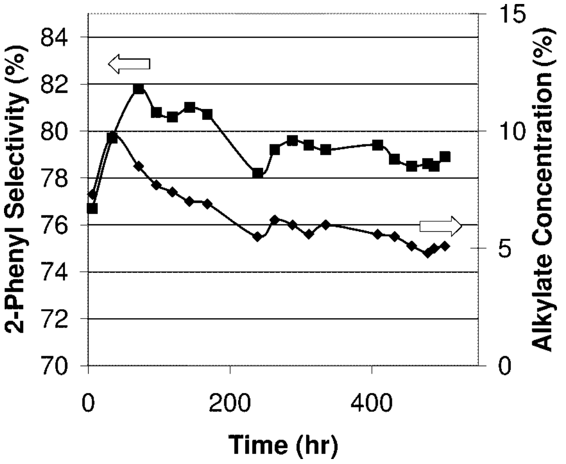


Figure 4. Benzene alkylation with C_{10}–C_{14} paraffin dehydrogenate catalyzed by fluorinated mordenite. (■) 2-phenyl selectivity (%) and (♦) alkylate concentration (%).

taneous 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 table 2).

Figure 3 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 [7].

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 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 3. 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 [16]. McVickers *et al.* report that severe fluoridation also leads to the conversion of non-framework aluminum species to AlF_3 [17].

Catalyst lives well in excess of 500 h on stream have been demonstrated with the fluorided 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 figure 4. 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 [16]. 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 lifetimes in C_{12}–C_{14} paraffin dehydrogenate/benzene service of >3000 h have been demonstrated.

References

[1] *Encyclopedia of Chemical Technology*, Vol. 2 (Wiley, New York) p. 58.

[2] *Chemical Economics Handbook* (Stanford Research Institute International, 1999).

[3] R.J. Larson, T.M. Rothgeb, R.J. Shrimp, T.E. Ward and R.M. Ventullo, J. Am. Oil Chem. Soc. 70 (1993) 645.

[4] T. Imai, J.A. Kocal and B.V. Vora, Sci. Technol. Catal. (1994) 339.

[5] H. Ming-Yuan, L. Zhonghui and M. Enze, Catal. Today 2 (1988) 321.

[6] J.H. Clark, G.L. Monks, D.J. Nightinggale, P.M. Price and J.F. White, J. Catal. 193 (2000) 348.

[7] C. Travers, F. Raatz, B. Juguin and G. Martino, Eur. Patent 466558 (1992) to Institute Francais du Petrol.

[8] Y. Cao, R. Kessas, C. Naccache and Y.B. Taarit, Appl. Catal. 184 (1999) 231.

[9] Z. Da, P. Magnoux and M. Guisnet, Catal. Lett. 61 (1999) 203.

[10] L.B. Young, US Patent 4 301 317 (1981) to Mobil Oil Corp.

[11] J.F. Knifton, P.R. Anantaneni and M. Stockton, US Patent 5 770 782 (1998) to Huntsman Petrochemical Corp.

[12] J.F. Knifton and P.R. Anantaneni, US Patent 5 777 187 (1998) to Huntsman Petrochemical Corp.

[13] J.F. Knifton, P.R. Anantaneni and P.E. Dai, US Patent 5 847 254 (1998) to Huntsman Petrochemical Corp.

[14] J.F. Knifton and J.C. Edwards, Appl. Catal. 183 (1999) 1.

[15] A. Kurosaki and S. Okazali, Bull. Chem. Soc. Jpn. 63 (1990) 2367.

[16] J.F. Knifton and J.C. Edwards, unpublished results.

[17] S. Soled, G.B. McVicker, J.J. Ziemiak, G. DeMartin, L. Yacullo, K. Strohmaier and J. Miller, in: *Division of Petroleum Chemistry, Preprints*, 206th Am. Chem. Soc. Meeting, Chicago, 1993, p. 546.