Synthesis of 2,6-Dimethylnaphthalene from Pentenes and Toluene

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Introduction
There has been recently worldwide increasing interest in the production of polyethylene naphthalate (PEN). PEN is produced by reacting 2,6-naphthalene dicarboxylic acid (2,6-NDCA) with ethylene glycol. PEN provides superior strength and heat resistance compared to polyethylene terephthalate (PET) in applications such as photographic film, fibers, containers and molded parts and has, hence, unique commercial advantages.

2,6-Dimethylnaphthalene (2,6-DMN) is a precursor for 2,6-NDCA manufacture. The production of 2,6-NDCA is similar to that of terephthalic acid in that a 2,6-dialkylnaphthalene (e.g., 2,6-DMN) is oxidized to the corresponding acid by using well established methods. Thus, the challenge lies in the manufacture of 2,6-dialkynaphthalenes, especially 2,6-DMN.

Based on the migration chemistry of the methyl groups on the naphthalene ring, the 10 DMN isomers are grouped into 4 triads: (i) 2,6-triad: 2,6-, 1,6- and 1,5-DMN; (ii) 2,7-triad: 2,7-, 1,7- and 1,8-DMN; (iii) 1,4-triad: 1,4-, 1,3- and 2,3-DMN, and (iv) 1,2-triad: 1,2-DMN alone. Producing 2,6-DMN is challenging, both sterically and economically, due to the following facts: (1) the positions of the methyl groups on the naphthalene ring make them difficult to control, (2) only two DMN isomers of 2,6-triad (1,6- and 1,5-DMN) can be efficiently isomerized to give the desired 2,6-DMN while the other 7 DMN isomers cannot, (3) the separations of 2,6-DMN from other 9 DMN isomers also require complicated processes.

Many conventional routes have been developed for producing 2,6-DMN, for example, (1) alkenylation/cyclization/dehydrogenation, starting with a monocyclic aromatic and a diolefin, (2) reforming/recovery from kerosene fractions, (3) recovery from cycle oil produced in fluid catalytic cracking (FCC) operations, (4) transalkylation of naphthalene with polyalkylbenzenes, and (5) methylation of naphthalene. However, all these approaches lack in economic efficiency for largescale production due to the facts mentioned above. In this paper we report a new technology of more efficiently synthesizing 2,6-DMN and demonstrate that a new technical breakthrough has been made by developing new chemistry [1,2]. Our process uses pentenes and toluene as low cost feedstocks. The output of 2,6-DMN is maximized through a novel hydroisomerization-dehydrogenation sequence. The properties of the catalysts employed in this technology will be discussed.

Results and Discussion
In the conventional routes, for example, the investigators alkenylate toluene with 1,3-butadiene to make ortho-pentenyltoluene over a base catalyst. The resulting ortho-pentenyltoluene is cyclized to 1,5-dimethyltetralin which is then dehydrogenated to 1,5-DMN. Since 1,5-DMN belongs to the 2,6-triad, 1,5-DMN readily isomerizes to
2,6-DMN over an acid catalyst. This route is depicted in Figure 1. To avoid making DMNs other than 2,6-triad isomers, this approach starts with more expensive ortho-xylene and 1,3-butadiene as feedstock and proceeds with more expensive base catalysis. Apparently, economically more efficient technologies are desirable.

Our new technology is presented in Figure 2. The process starts with less expensive toluene and pentenes as feedstocks. Toluene is alkylated with pentenes over a less expensive acid catalyst such as zeolite Y to make pentyltoluenes (PT). The PTs are then converted to a mixture of 2,6-/2,7-triad DMNs over a conversional reforming catalyst such as Pt/Re/Al₂O₃. For example, at ~100% PT conversion, ~80% DMNs was produced with 2,7-, 1,7-, 2,6-, 1,6- and 1,5-DMN in about a 2:2:2:2:1 ratio. In the subsequent hydroisomerization step over a bifunctional catalyst containing both hydrogenation/dehydrogenation function (e.g., highly dispersed Pt or Pd) and acidity (e.g., zeolite), at least one aromatic ring of DMNs is saturated. Saturating makes the “inter-triad” migrations of methyl groups of the resulting dimethyltetralins (DMT) and/or dimethyldecalins (DMD) over an acid catalyst much easier by allowing for positional shifts that were prohibited by the DMN triad chemistry when both rings are aromatic. Dehydrogenating the isomerized DMT-DMD mixture (including the resulting 2,6-DMT and/or 2,6-DMD) produces an appreciable level of desirable 2,6-DMN from not only 2,6- but also 2,7-triad DMNs. The unconverted DMNs other than 2,6-DMN are recycled to the hydroisomerization step to boost the 2,6-DMN yield. For example, when 2,7-DMN was hydroisomerized over a Pd/beta zeolite catalyst and the resulting products were dehydrogenated over a Pt/Na-ZSM-5 catalyst, the DMN recovery was 97% and 36% 2,6-DMN was yielded.

References