PART I

SYNTHESIS, CHARACTERIZATION, AND BASE CATALYSIS OF NOVEL ZEOLITE SUPPORTED SUPER—BASIC MATERIALS

CHAPTER 2

INTRODUCTION

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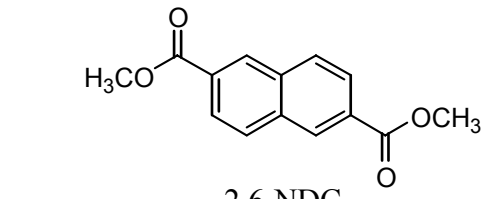
2.1 Overview

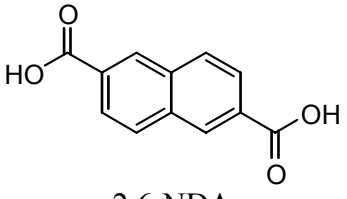
Zeolites are most well known for their adsorption, separation and acidic properties in the petroleum and chemicals industry.[1] The basic properties of zeolites are less well understood, although many syntheses could benefit from the shape selectivity afforded by zeolite supported base catalysts. Since the discovery of Pines et al. that sodium metal supported on alumina is active for the double-bond migration of olefins,[2] there has been an interest in heterogeneous base catalysis and thus the basic properties of zeolites.[3-5] The presence of carbanions during base catalysis results in product profiles not easily obtainable by acid catalysis and desirable in fine chemical synthesis. Base catalyzed reactions of particular interest are the double bond isomerization of olefins, side chain alkylation of aromatics, dehydrogenation of alcohols, Michael additions, and the Knoevenagel condensation of aldehydes.[6-17] This study, however, focuses on the generation of a novel zeolite supported super-base capable of shape selective carbon-carbon olefin addition to alkyl aromatics. The industrially relevant alkenylation of *o*-xylene with 1,3-butadiene to produce 5-ortho-tolyl-pent-2-ene (5-OTP) is currently catalyzed over sodium-potassium eutectic[18] and is used as a probe reaction due to its requirement of very strong basic sites. The product 5-OTP is a precursor to the valuable high performance polyester polyethylene naphthalate (PEN).

2.2 An industrial application: Production of polyethelene naphthalate

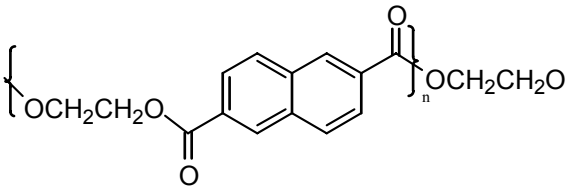
Polyethylene naphthalate (PEN) is a high—performance, thermoplastic polyester that effectively fills the performance gap between polyethylene terephthalate (PET) and high priced, high performance polyimide and polyamide films. The structures of PEN, its precursors dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and 2,6-naphthalenedicarboxylic acid (2,6-NDA), and PET are given in Figure 2.1. Due to its naphthalate double ring structure, PEN exhibits superior thermal, mechanical, electrical, and chemical barrier properties over its terephthalate and benzene ring counterparts, as illustrated in the comparison between PEN and PET films (Table 2.1).[18] Consequently, several companies have expressed interest in PEN. Goodyear hoped to use PEN fibers for tire radial belts, while 3M was interested in using PEN for magnetic recording tape. Furthermore, because of its superior permeability and thermal properties, there has been a large interest in PEN for packaging applications. Plastic beer bottles, improved carbonated beverage containers and hot fill containers are some examples of PEN's packaging applications.



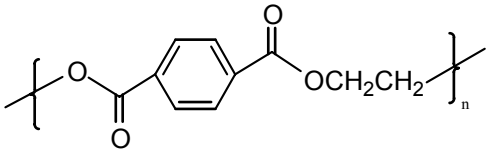
2,6-NDC



2,6-NDA



Polyethylene Naphthalate (PEN)



Polyethylene Terephthalate (PET)

Figure 2.1: Structure of polyethylene naphthalate (PEN) and its precursors dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and 2,6-naphthalenedicarboxylic acid (2,6-NDA) in comparison to polyethylene terephthalate (PET).

Property	**PEN**	**PET**
Young's Modulus (Mpa)	5200	3900
Glass Transition (^{o}C)	122	80
Thermal Rating (^{o}C)	155	105
Oligomer Extraction (mg/m^2)*	0.8	20
Hydrolytic Resistance (hr)†	200	50
Radiation Resistance (MGy)‡	100	2
Thermal Shrinkage (%)#	0.6	1.3
Oxygen Permeability (cm^3/m^2/day/atm)+	20	56

* 1 hr in chloroform @ 23^{o}C
† time to retain 60% elongation at 130^{o}C
‡ dose to retain 50% elongation to γ-rays in vacuum
# 30 min at 150^{o}C
+ 25μm film

Table 2.1: Properties and PEN and PET films, adapted from reference [18].

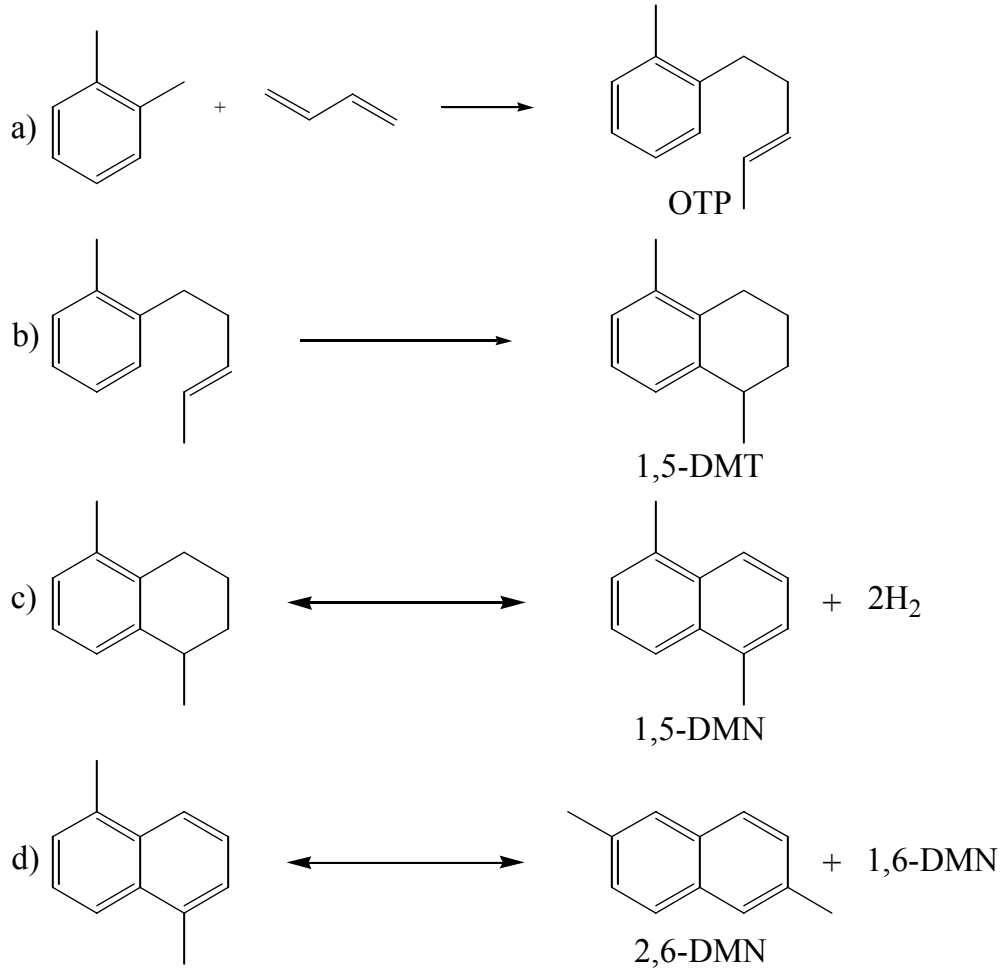
The first world scale plant for the production of PEN was constructed in 1995 by BP-Amoco, testifying to the large difficulties involved with successful commercialization of a PEN production process. Further large scale production is restricted by the production cost of the PEN precursors, dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and 2,6-

naphthalenedicarboxylic acid (2,6-NDA) (Fig. 2.1). Hence, the use of PEN is currently limited to specialty applications. The enormous potential market for PEN, however, has driven research towards the efficient synthesis of 2,6-NDA and 2,6-NDC for decades.

Several routes to the synthesis of PEN precursors have been investigated. Even before the semi-commercial introduction of PEN to the marketplace in 1970 by Teijin, a significant amount of research had been devoted towards the development of an economical process for the production of 2,6-NDC and 2,6-NDA.[18] The first attempts at 2,6-NDC and 2,6-NDA production were based on refinery stream isolation of monomethyl naphthalenes from naphthalene production feedstock. These endeavors were quickly abandoned due to lack of adequate supply. Several synthetic routes were subsequently investigated, including di-iodonaphthalene carbonylation, transcarboxylation of naphthalene, alkyl aromatic acylation, alkyl aromatic base-catalyzed condensations, and various aromatic alkylations. These routes and others are discussed in detail elsewhere.[18] Most of these syntheses were abandoned due to poor economics or environmental concerns.

The route chosen by BP-Amoco for the production of 2,6-NDA and 2,6-NDC is the oxidation of 2,6-dimethyl naphthalene (2,6-DMN). 2,6-DMN can be produced by the alkenylation of *o*-xylene with 1,3-butadiene to 5-OTP followed by subsequent cyclization, dehydrogenation, and isomerization. The four-step BP-Amoco reaction scheme to 2,6-DMN is shown in Scheme 2.1. This scheme allows the commercial production of 40,000 tons per year of 2,6-NDA. Despite BP-Amoco's success in commercialization of the 2,6-NDA process, the cost of PEN remains prohibitive for general application use mainly due to difficulties in the first step of 2,6-DMN synthesis, the alkenylation of *o*-xylene with 1,3-

butadiene. The remaining steps are all high yield, high selectivity reactions. The difficulty associated with alkenylation of *o*-xylene with 1,3-butadiene is due to the requirement of a very strong basic site to catalyze the reaction. Conventional bases, such as alkali—metal oxides and alkali—metal exchanged zeolites are not powerful enough for the alkenylation reaction. Thus, the catalyst used in the process is a bulk sodium-potassium eutectic alloy of 22 wt% sodium and 78 wt% potassium.[18] Aside from the obvious handling and safety issues associated with using such a reactive catalyst, the NaK alloy is not highly selective to 5-OTP. As a result, conversion of the alkenylation reaction is limited to 10% with a large recycle to ensure a high selectivity to 5-OTP.

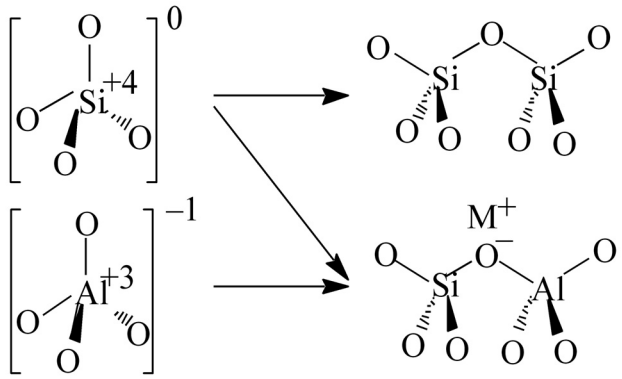


Scheme 2.1: Sequential production scheme for 2,6-DMN; a) alkenylation, b) cyclization, c) dehydrogenation, d) isomerization. 2,6-DMN is subsequently oxidized to 2,6-NDA.

2.3 Zeolites as basic catalysts

Zeolites are microporous crystalline materials formed from the condensation of SiO_4 and AlO_4^- tetrahedra (Scheme 2.2). The aluminum tetrahedra result in negatively charged oxygen atoms within the framework of the zeolite which are balanced by cations, often in the form of alkali—metal ions. The negatively charged oxygen centers act as base sites within the zeolite. The number of alumina tetrahedra present in a given zeolite, and

thus the number of framework base sites, can be controlled during synthesis or modified post-synthesis by de-alumination.[19]



Scheme 2.2: Condensation of SiO_4 and AlO_4^- tetraheda to form the alumosilicate framework of a zeolite.

Various methods of modifying the nature of alkali—metal cations have been used to vary the basic strength of oxygen in the zeolite framework. A summary of alkali—metal modified zeolites and the base reactions they catalyze is presented in Table 2.2. The most straightforward way to adjust the basic strength of the oxygen centers is to vary the balancing cation of the oxygen. The more electropositive the cation, the more basic the oxygen site will become. This approach yields only weakly basic materials. Basicity of the material can be increased by occluding alkali—metal oxides within the pores of the zeolites by thermal decomposition of a previously impregnated alkali—metal precursor such as the corresponding acetate salt.[7,10,15,20,21] The resulting zeolite occluded alkali—metal oxides are capable of base catalyzed 1-butene isomerization, side-chain alkylation of aromatics with methanol and dehydrogenation of alcohols. These basic materials, however, are unable to activate aromatics for side-chain olefinic alkenylation.[15,21,22]

Increasing base strength ↓

Type of Zeolite	Catalyzed Reactions	References
Alkali-ion exchanged	butene isomerization	15,20
	alkylation of toluene with methanol	6,11,16
Occluded alkali-oxide	butene isomerization	20,21
	Knoevenagel condensation	10
	Michael addition	12,23
	dehydrogenation of isopropanol	15,24,25
Occluded alkali—metal clusters	butene isomerization	21,26
	aldol condensation	27
	alkenylation of aklylbenzenes	21,25,27

Table 2.2: Base catalyzed reactions facilitated by alkali—metal modified zeolite supports.

Unlike occluded alkali—metal oxides, occluded alkali—metal clusters are capable of side-chain alkenylation of aromatics. Using sodium occluded in faujasite, for example, ethylation of toluene, ethylbenzene and *i*-propylbenzene has been demonstrated over a fixed bed, gas phase reactor.[21,27] Alkenylation of *o*-xylene with 1,3-butadiene over cesium- and sodium-occluded faujasites has also been demonstrated, although it was performed in a semi—batch reactor.[22,25] In this report, cesium and sodium occluded within the pores of zeolite X were catalytically active for alkenylation of *o*-xylene with 1,3-butadiene to yield 5-OTP, but were not nearly as active as bulk potassium in the semi—batch phase. Occluded potassium was not studied. A summary of these data are collected Table 2.3. The catalytic behavior of the occluded sodium is particularly interesting, since bulk sodium does not catalyze the alkenylation reaction in the time frame studied. The discontinuity between the bulk and occluded behavior of sodium is not completely surprising, however, since various other studies have found discrepancies between bulk and occluded behavior. As an example, ^{133}Cs NMR has been used to show that cesium-oxide occluded in zeolite Y experiences a vastly different electronic environment than bulk cesium-oxide.[20] Similarly, Li et al. used temperature programmed reduction to show that the chemical properties of

mixed Sb-V oxides supported in zeolite beta are vastly different than their bulk analogues.[28] Based on the results of Davis and co-workers and the unusual properties of confined species compared to their bulk analogues, it seems that occlusion of potassium metal or sodium-potassium alloys within the zeolite could result in novel zeolite supported materials capable of the alkenylation of *o*-xylene with 1,3-butadiene, and generally, of the carbon-carbon addition of olefins to alkyl aromatics. It is with this in mind that the present study was initiated.

Catalyst	Turnover Number	Conversion	Selectivity to 5-OTP
Na metal	-	-	-
K metal	43.3	10.5	91.6
NaN_3/NaX	5.5	3.9	86.4
CsN_3/NaX	12.3	13.9	89.9
NaN_3/KX	14. 0	9.2	85.3

Table 2.3: The alkenylation of *o*-xylene with 1,3-butadiene over alkali—metal occluded zeolite X as reported by Davis and co-workers.[22,25]

Several other methods for modifying the basic properties of zeolites are discussed in the review by Weitkamp, Hunger, and Rymsa.[3] Impregnation of sodium exchanged zeolite Y with liquid lanthanides in ammonia, followed by calcination results in amide and imide species within the pores of the zeolite. These lanthanide catalysts have been shown active for double-bond isomerization of butenes. Additionally, organic bases may be incorporated into zeolites. When *N,N'*-dicyclohexylcarbodiimide is reacted with cyclohexylamine in the supercages of dealuminated zeolite Y, encapsulated *N,N',N"*-tricyclohexylguanidine is formed and is too large to diffuse from the interior cages of the

zeolite. This particular "ship-in-a-bottle" technique results in only weakly basic materials unsuitable for use in the current study. Additionally, basic activity for Knoevenagel condensation due to terminal $–NH_2$ and –NH groups has been observed in faujasites treated with ammonia at high temperature.[17] These catalyst, however, do not posses the required base strength to be included in this study.

2.4 Strategy for the synthesis of a novel zeolite supported super-base

Due to reports that strongly basic catalysts can be formed from the occlusion of alkali—metals within zeolite pores,[22,25-27,29] this system is adapted in the current study in the search for a new zeolite supported super-base catalyst. Alkali—metal clusters can be occluded within the zeolite pores by vapor deposition,[30,31] or by in-situ decomposition of previously impregnated alkali—metal azides.[21,25-27,29,32-34] Electron paramagnetic resonance (EPR) shows that following azide decomposition in faujasite, three distinct types of sodium particles are present: extralattice Na_x^o, intracrystalline Na_y^o, and ionic Na_4^{3+} clusters encapsulated in the sodalite cages.[26,35] The relative population of neutral intracrystalline sodium and sodalite encapsulated ionic clusters is affected by the decomposition heating rate. Slow decomposition at 1K/min gives rise to intracrystalline clusters while fast heating at 25K/min gives rise to ionic clusters.[26] It was found that oxygen atoms in the neighborhood of neutral intracrystalline sodium clusters are the active centers for base catalysis, indicating that slow decomposition is preferred.[27]

Since occlusion of an alkali-alloy within the zeolite will require controlled deposition of metal precursors, the alkali azide method of impregnation reported Martens

and co-workers is well suited for this study. Methanolic impregnation and subsequent thermal decomposition of mixed alkali—metal azides may allow for alloy formation within the zeolite pores. Failing this, several studies have reported the formation of alkali-alloys within zeolite cavities by vapor deposition of an alkali—metal into a zeolite containing a different ion-exchanged alkali—metal. The metal in the vapor phase is able to exchange electrons with the ion-exchanged alkali-ions in the zeolite framework, creating metal clusters from the exchanged ions.[31,36,37] Further vapor phase metal then diffuses into the clusters, creating an alloy.[38,39] As alkali—metal vapor may be present during the thermal decomposition of alkali—metal azides in zeolites,[16] alloys might also be formed during thermal decomposition of materials prepared by the azide impregnation method. Additionally, alkali—metal alloys may be formed by high temperature annealing of decomposed alkali azides in zeolites exchanged with different alkali—metal ions. In an EPR study, it was shown that cesium and mixed cesium/sodium clusters were formed in cesium exchanged zeolite Y after decomposition of sodium azide.[37] The mechanism proposed for this phenomenon involves diffusion of sodium clusters from the external surface into the zeolite followed by electron exchange and subsequent clustering of the cesium cations. The mechanism is very similar to that observed in the vapor phase described previously.

Prior art indicates that alkali—metal alloys can be created within the pores of zeolites. Furthermore, the use of alkali—metal azides as precursors allows control over the amount and type of metal clusters or alloys formed within the pores. Due to extensive research of ionic alkali—metal clusters within the pores of various zeolites,[40] the systems are well understood and characterization techniques are well documented. Thus, alkali—

metal azide impregnation of zeolite X provides a rich platform for the synthesis of a new zeolite supported basic catalyst capable of carbon-carbon addition to alkyl aromatics.

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