

Deactivation of nitrile hydrogenation catalysts: New mechanistic insight from a nylon recycle process

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Abstract

In the recycling of nylon-6 and nylon-6,6, high temperature ammonolysis leads to reversion of the polymers to monomer units and dehydration of amide monomers to nitrile molecules. The resulting product is a mixture of 6-aminocapronitrile, caprolactam, adiponitrile, hexamethylenediamine and other species. To complete the recycle loop the nitrile molecule can be hydrogenated to hexamethylenediamine. This liquid phase hydrogenation has been studied over Raney[®] Ni and Raney[®] Co catalysts at less than 100 °C and 3.5 MPa in semi-batch mode. Raney[®] Ni exhibited rapid deactivation in the absence of sodium hydroxide, while Raney[®] Co provided long catalyst life. In comparison studies, Raney[®] Ni also deactivated during hydrogenation of pure adiponitrile, in the absence of sodium hydroxide. While sodium hydroxide inhibits Raney[®] Ni deactivation, it presents an economic and environmental challenge for waste handling. Analysis of recovered catalyst samples by ESCA showed an increase in nitrogen and carbon on the surface of deactivated Raney[®] Ni samples compared to recovered Raney[®] Co and control samples. The observed overlayer was consistent with the formation of oligomeric secondary amines, which covered the catalyst surface and prevented further reaction. Amine coupling reactions were favored for Raney[®] Ni compared to Raney[®] Co.

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1. Introduction

Recycling of waste nylon carpets has become an increasingly important problem in recent years [1] since landfill capacity is nearing maximum utilization and nylon fibers can last 30–40 years in conventional landfills [2]. In the United States, a minimum of 25% recycle content is required in government carpet installations, and major fiber producers have developed and/or commercialized recycling processes. Carpet waste generally includes both industrial carpet waste and post-consumer carpet waste. Challenges to carpet recycling include not only the logistic of collection and distribution but also the complexity of materials used in carpet construction. Carpet may include the carpet facing polymer such as nylon or polypropylene, as well as the dyes, adhesives, compounding

and backing materials such as rubber, polyurethane and even calcium carbonate. Furthermore, nylon polymers present a critical problem arising from their high melting point and low solubility. These characteristics, which are valued for producing high quality carpets, lead to challenges to recycling processes. While recycling of some polymers such as polystyrene and polyethylene may rely on dissolution or melting, many nylon recycling processes rely on conversion of the polymer back to monomer for effective recycling.

The nylon recycle process for recovering monomers from post-industrial and post-consumer nylon-6 and nylon-6,6 carpet fibers is a multistep operation. A plethora of depolymerization processes have been explored in past laboratory studies, including steam stripping, water hydrolysis, nitric acid hydrolysis, and acetic acid acetolysis [3], but depolymerization via ammonolysis has been shown to be a technically feasible route for the recovery of high purity nylon intermediates [4].

In the ammonolysis process (Fig. 1), first the recovered carpets are mechanically separated to remove the carpet backing and latex from the nylon fiber. The nylon (-6 and/or -6,6) fiber is

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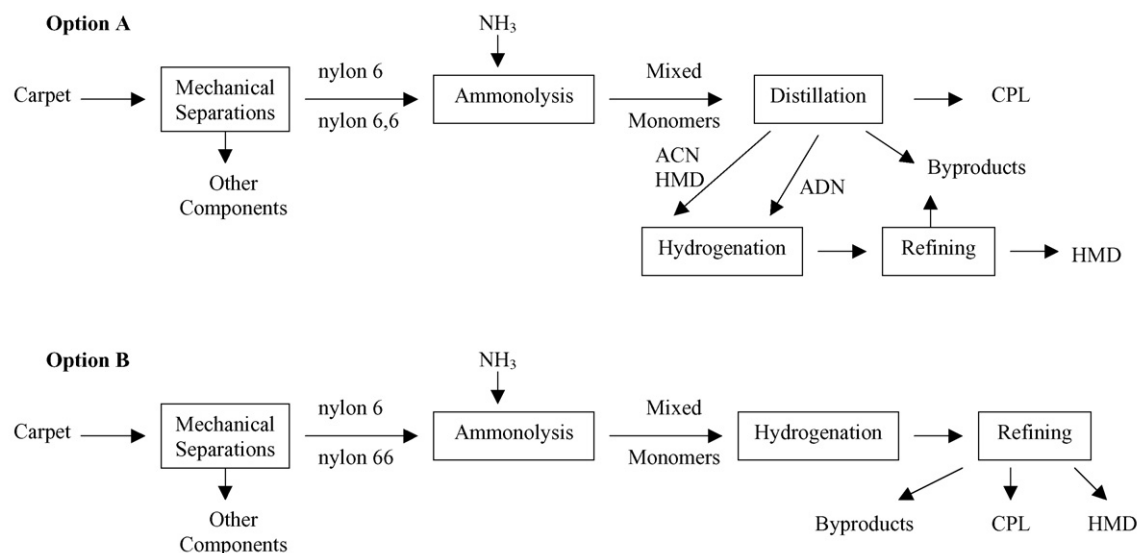


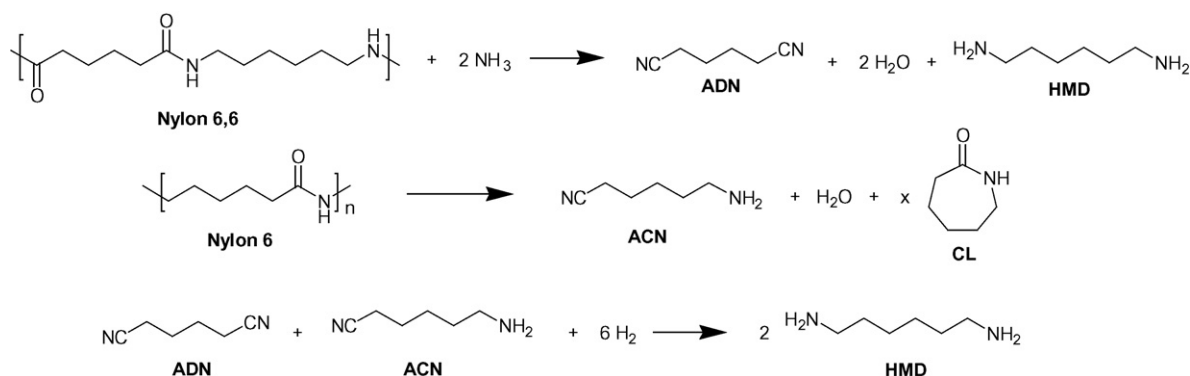
Fig. 1. Block diagram of nylon-6 and -6,6 recycling process. ADN, adiponitrile; ACN, 6-aminocapronitrile; HMD, hexamethylenediamine; CPL, caprolactam.

then depolymerized at elevated temperature and pressure in the presence of excess ammonia to form a mixture of monomers. In this chemistry, the secondary amides of the nylon polymers react with ammonia to break the nylon chain and form a primary amide and an amine. The primary amide can subsequently be dehydrated to form a nitrile group. The resulting ammonolysis product is predominantly a mixture of four major components. Hexamethylenediamine (HMD) and adiponitrile (ADN) are formed from nylon-6,6, while 6-aminocapronitrile (ACN) and caprolactam (CPL) are formed from nylon-6 (Scheme 1). In addition to these major components, several degradation products and products from incomplete reaction remain, including 5-cyanovaleamide, 6-aminocaproamide and low molecular weight oligomers. The ammonolysis product may subsequently be separated by distillation into components, followed by hydrogenation of the components to make HMD or the ammonolysis product may be directly hydrogenated to form HMD, CPL and other products. CPL remains intact during the hydrogenation reaction. The crude recycled HMD and CPL can be separated by distillation and subsequently refined to produce monomer grade HMD and CPL, respectively. The CPL can be directly polymerized to

nylon-6 or it can be recycled back to the ammonolysis reactor, where it can be converted into ACN.

A significant factor impacting the feasibility of the nylon recycle process is the productivity or lifetime of the hydrogenation catalyst. Nitrile hydrogenation catalysts are known to deactivate. For acetonitrile hydrogenation in the gas phase over nickel catalysts, the deactivation has been attributed to a nitrile “cracking” mechanism, which leads to an unreactive nickel carbide surface [5]. We, recently, investigated the deactivation of Raney Ni catalysts during liquid phase nitrile hydrogenation and suggested an alternate deactivation mechanism [6]. Rather than a “cracking” mechanism, we suggested that amine condensation reactions lead to insoluble oligomers, which adsorb to active catalyst sites and prevent further reaction. The mechanism was consistent with three key observations:

- Deactivation was observed for α,ω -dinitriles, while mononitriles such as hexanenitrile showed no deactivation.
- The only mononitriles that did exhibit deactivation were aminonitriles, which are capable of participating in amine condensation oligomerization.



Scheme 1. The idealized ammonolysis and hydrogenation chemistries of nylon-6,6 and nylon-6 recycle.

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