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The ammonolytic hydrogenation of secondary amides: an efficient method for the recycling of long-chain polyamides

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PURPOSE OF THE ABSTRACT

Polyamides (PAs) are important engineering plastics that are used in a plethora of durable applications as a result of their high stability. PA6 and PA66 are often used for more general purposes (e.g. carpet) while long-chain polyamides (LCPAs) are more expensive with better mechanical properties and therefore mainly useful in specialized niche applications (e.g. water pumps). However, this high stability and durability are obstacles when dealing with end-of-life PA wastes. Typically, one can deal with plastic waste via either landfilling, waste-to-energy (WtE) or recycling. Landfill is no longer acceptable; and for high value plastics it would be highly inefficient to burn the material and generate some electricity in the process, while continuing to produce virgin plastic from a mostly crude oil based feedstock. [1] This is particularly the case for nitrogen containing plastics such as polyamides, which in addition to typical greenhouse gases (i.e. CO2), also release NOx gasses . Recently, some progress has been made on the chemical recycling of PA6 and PA66 [2, 3], but often harsh reaction conditions in combination with homogeneous catalysts have to be applied to obtain moderate yields. Research on the ammonolysis of LCPAs is, however, scarce. Here, a new chemocatalytic ammonolysis process for LCPAs was developed, which can operate under relatively mild conditions and uses cyclopentyl methyl ether (CPME) as a green solvent.

The ammonolysis of N-hexylhexanamide, a model component for polyamides, was initially investigated. Niobium oxides (Nb2O5 and Nb2O5?H2O) were found to be effective heterogeneous catalysts. After a reaction time of 5 hours, a conversion of 36% was achieved with Nb2O5 (initial reaction conditions: 0.1 M reactant, 200 °C, 6 bar NH3, 1 bar H2 in CPME). Further kinetic experiments suggested that the ammonolysis reaches an equilibrium conversion (i.e. 45%) after 24 hours. Aside from the ammonolysis, niobium oxides also catalyzed the dehydration of primary amides. Next, the reaction parameters were optimized in presence of the best performing Nb2O5: CPME was proven to be the most suitable solvent. The influence of the temperature was again two-fold; a higher temperature resulted in an increased conversion and increased the reaction equilibrium constant. Additionally, higher NH3 pressures gave rise to increased reaction rates and equilibrium conversions. Based on these findings, a reaction mechanism was proposed in which Lewis acid and Brønsted acid sites, both present on the catalyst's surface, effect the ammonolysis of secondary amides.

In a second stage, the ammonolysis was coupled to a hydrogenation process to convert the generated primary amides to primary amines. This resulted in a bicatalytic (combining Nb2O5 and RuWOx/MgAl2O4) ammonolytic hydrogenation process with optimal conditions: 200°C, 6 bar NH3, 50 bar H2 with CPME as a green reaction solvent. As such, actual plastic samples (i.e. PA 1010, PA 11 and PA 12) were completely depolymerized, leading to ?,?-diamines. The process was proven to be robust against common impurities (e.g. plasticizers, antioxidants, other plastic contaminations and fillers). However, any sulfur-containing compounds must be removed in order to maximize the lifespan of the Ru-catalyst.

In conclusion, it was shown that Nb2O5 is an excellent heterogenous catalyst for the ammonolysis of secondary amides. The combination of the ammonolysis (i.e. Nb2O5) with a hydrogenation (i.e. RuWOx/TiO2) results in a robust system for the chemical recycling of PA, mainly LCPA.

FIGURES

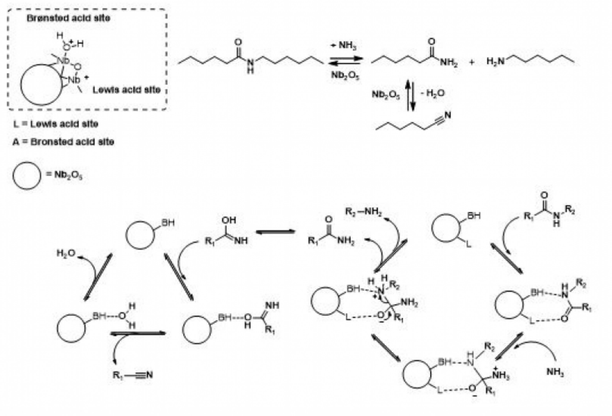

FIGURE 1

Figure 1

Ammonolysis of N-hexylhexanamide to hexanamide and hexylamine coupled to the dehydration of hexanamide to hexanenitrile (top). Proposed reaction mechanism for the ammonolysis of a secondary amide and the dehydration of a primary amide with a Nb2O5 catalys

FIGURE 2

KEYWORDS

heterogenous catalysis | secondary amides | ammonolysis | polymer recycling

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