



Original research article

Removal of toxic HCN and recovery of H₂-rich syngas via catalytic reforming of product gas from gasification of polyimide over Ni/Mg/Al catalysts



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ABSTRACT

The recycling of *N*-containing plastics by pyrolysis or steam-reforming is typically complicated by the generation of toxic HCN. In this study, polyimide, as an example of an *N*-containing plastic, was gasified and the product gas was reformed over various Ni/Mg/Al catalysts. Effects of catalyst properties, steam, and temperature on the HCN removal and H₂-rich syngas production were investigated. More than 99% HCN removal (compared with pyrolytic conditions) and ~3000 mL g⁻¹ of H₂-rich syngas with a H₂/CO ratio of 10.4 were simultaneously achieved at 800 °C in the presence of a reduced-Ni_{1.0}Mg_{3.6}Al_{4.8} catalyst, then HCN was mainly converted into N₂. On the other hand, non-reduced same catalyst enhanced hydrolysis of HCN into NH₃ with more than 98% HCN removal at 800 °C, which is also a beneficial finding to recover useful NH₃ from HCN, directly. Therefore, the present work achieved that the improvement of the H₂-rich syngas yield and quality, and conversion of toxic HCN into non-toxic N₂ or useful NH₃ using the same catalyst, simultaneously.

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1. Introduction

The development of recycling techniques for *N*-containing plastic wastes such as polyamide, polyimide, and polyurethane is highly desirable for improving the recycling rate of waste plastics and advancing plastic recycling technology to the next level. Waste plastics are mainly generated during the manufacturing process or at the end of a product's useful life. In the first case, the structure and composition of the plastic are well known, and because they are collected in a relatively homogenous state, mechanical recycling or solvolysis as feedstock recycling methods are suitable treatments. Solvolysis can convert the wastes into not only the respective monomers but also valued-added chemicals at comparatively low temperature [1–8]. For example, Kamimura et al. [1,2] achieved the high-yield recovery of ω-hydroxyalkanoic acids from nylon-6 and nylon-12 using supercritical MeOH at ~300 °C, which are important intermediates in the chemical industry, costing more than twice as much as virgin caprolactam. Thus, solvolysis is one of the best ways to treat highly pure plastic wastes. In contrast, plastics collected at the end of a product's lifecycle are often

combined or mixed with resins, metals, and other additives, and collecting high purity plastics is extremely difficult. These contaminants negatively impact the product purity as well as the possibility of extended solvent use.

Pyrolysis is a well-known technique that avoids the use of solvents and requires only heat to cleave the polymer chains, decomposing both plastics and organic additives into gases and oils. Therefore, it is suitable for treating waste plastics that cannot be treated by mechanical recycling and solvolysis. Our previous work revealed that the addition of steam during the pyrolysis of a polyimide film (Kapton) at 900 °C and atmospheric pressure simultaneously produced H₂- and CO-rich syngas and a highly porous activated carbon (Brunauer-Emmett-Teller (BET) surface area = 1874 m² g⁻¹). In contrast, the normal pyrolysis of polyimide produces low-value CO- and CO₂-rich gas with extremely low porosity carbon char [9]. Therefore, the previous work indicated that steam gasification is one of the best ways to recover syngas and activated carbon from *N*-containing plastic wastes. Unfortunately, the production of toxic hydrogen cyanide (HCN) is unavoidable during the pyrolysis of *N*-containing plastics [10–14]. HCN is one of the most dangerous toxic gases, fatal to humans at a concentration of 300 ppm for 1 min [15]. According to the World Health Organization (WHO), an HCN concentration of 4.7 ppm is the occupational exposure limit [16].

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Generally, in an industrial process, HCN is absorbed into aqueous solution where it is treated by alkaline chlorination [17,18] or oxidation [19–24]. The addition of an HCN treatment facility in-line with the gasification process increases the operational costs and process complexity. Therefore, direct HCN decomposition during the gasification process would be desirable.

HCN removal over heterogeneous catalysts has been investigated. The oxidation of HCN by air in the presence of precious metal-loaded catalysts such as Pt-supported Al_2O_3 [25] or Pt-, Pd-, and Rh-supported TiO_2 pellets [26] has been reported. However, the oxidation process requires additional air as oxidant, which then dilutes the product gas with the added N_2 . The oxidation of HCN can also result in NO_x production. Therefore, the removal of HCN from the product gases by oxidation suffers from decreases in the process utilization efficiency and quality of the product gas. Further, the requirement for precious metal catalysts is disadvantageous in terms of resource conservation and cost.

Ni-based catalysts, as comparatively inexpensive noble metal catalysts, would be suitable candidates for the removal of HCN. They are well-known steam reforming catalysts for various pyrolysates derived from biomass [27–34], plastics [35–42], and their mixtures [43–45]. The effectiveness of Ni-based catalysts for removing HCN [46–53] by hydrogenation (Eq. (1)) and subsequent decomposition of NH_3 into N_2 (Eq. (2)) have been reported.



NH_3 is a well-known corrosive gas which can damage industrial equipment in the absence of special handling precautions. In addition, HCN and NH_3 are precursors of the NO_x species that can form during combustion and contribute to environmental pollution. On the other hand, NH_3 is an important basic chemical and fertiliser which is typically synthesized from H_2 and N_2 under severe conditions by the Haber–Bosch process, although recently, Showa Denko K. K. (Japan) has begun using an NH_3 synthesis process fed with syngas produced from the gasification of waste plastics (the KPR process) [54]. In summary, then, it can be concluded that HCN must be removed, but whether the same holds for NH_3 depends on the intended use of the syngas products and the features of the treatment facility. Therefore, the complete removal of HCN and control of NH_3 emissions in the produced syngas during a gasification process will be highly beneficial for the advancement of N-containing waste plastics recycling. However, the control of HCN and NH_3 emissions using Ni-based catalysts has not been achieved, and the influence of catalyst properties on HCN and NH_3 decomposition remains unclear.

To clarify these objectives, we focused on Ni/Mg/Al composites as heterogeneous catalysts, given their well-described catalytic activity in steam reforming. Both Al_2O_3 and MgO are well-known effective Ni supports [55,56]. We expected that not only the control of HCN and NH_3 emissions but also improvements in syngas quality by such catalysts could be investigated simultaneously. In this work, various types of Ni/Mg/Al catalysts were prepared to investigate the influence of catalyst properties on the production of HCN, NH_3 , and syngas. As an N-containing plastic, we selected the polyimide film, Kapton, for steam-gasification based on a prior investigation in which we confirmed that it produces H_2 - and CO-rich syngas containing HCN and NH_3 [9]. The HCN- and NH_3 -containing syngas produced by the steam-gasification of Kapton was further reformed by the synthesized Ni/Mg/Al catalysts in a fixed-bed reactor. The influence of catalyst properties, steam, and temperature on the system performance is discussed through a products distribution analysis and characterization of the catalysts.

2. Experimental

2.1. Materials

Kapton 200 V film (poly(4,4'-oxydiphenylene-pyromellitimide)) was purchased from Du Pont-Toray Co., Ltd. (Japan), and cut into 8 mm × 8 mm pieces. The elemental composition of this material was reported in our previous paper [9] as C, 67.8%; H, 3.0%; O, 22.0%; and N, 7.1%.

The catalyst starting materials $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, as well as other chemicals, were purchased from Kanto Chemical Co., Inc. (Japan).

2.2. Catalyst preparation

Catalysts with various Ni/Mg/Al ratios were prepared by the coprecipitation method described in our previous report [57]. Briefly, a solution of Ni, Mg, and Al nitrates (500 mL in defined molar ratios) was added dropwise into deionised water (500 mL) at 35 °C with 300 rpm agitation. The solution pH was kept at 10.5 by the dropwise addition of 1 M NaOH solution. The mixture was stirred for 2 h after terminating the nitrates solution addition. The precipitate was isolated by filtration, washed thoroughly with deionised water, and dried under reduced pressure (133 Pa) at 40 °C for 24 h. The dried precipitates were ground into powder using a mortar and pestle, and then were calcined at 800 °C for 3 h in air to produce the Ni/Mg/Al oxides. The calcined catalysts were ground, sieved, and used <250 μm particles for all reforming tests.

The composition of the fresh catalysts was determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES, Thermo Fisher Scientific Inc., iCAP 6500 Duo) following dissolution of the dried precipitates in 0.1 M HNO_3 . The fresh catalysts were characterized by X-ray diffraction (XRD, Rigaku powder diffractometer RINT-2200VHF+/PC, scanning between 3° and 90° using the Cu $\text{K}\alpha$ line), field emission-scanning transmission electron microscopy (FE-STEM, Hitachi-High-Technologies Corporation, HD-2700), and surface analysis (MicrotracBEL Corp., BELSORP-mini II). Temperature-programmed reduction (TPR) was carried out for fresh catalysts which are oxide state following the condition reported by Li et al. [32].

The used catalysts were characterized by XRD, scanning electron microscopy (SEM, Hitachi-High-Technologies Corporation, S-4800), and FE-STEM. Temperature-programmed oxidation (TPO) analysis was carried out following the condition reported by Kumagai et al. [43].

2.3. Steam-reforming experiments

The steam-gasification experiments were carried out using the fixed-bed reactor described in Fig. 1. The reforming conditions used in the present work are summarized in Table 1. Details of the equipment and procedure have been published elsewhere [9,58]. Briefly, a catalyst (500 mg) was set into the lower chamber. In the absence of catalyst, only quartz wool was set into the lower chamber. Next, the sample (500 mg) was fixed into the quartz sample holder, which was located at the top of the reactor (outside the furnace). The air inside the reactor was replaced by a constant helium flow of 150 mL min^{-1} for 30 min. When reduced catalysts were used (entries 12–17, Table 1), the helium gas flow was switched to H_2 gas flow at a flow rate of 30 mL min^{-1} at 800 °C, which was maintained for 60 min. After terminating the H_2 reduction pre-treatment, the H_2 inside the reactor was completely purged with helium. The upper furnace was heated to 900 °C and the catalyst chamber was set to the desired temperature. Then, steam was fed into the reactor at a flow rate of 150 mL min^{-1} to achieve a steam concentration of 50 vol% (He + steam = 300 mL min^{-1}). When a constant carrier-gas

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