

Article

Selective Production of Terephthalonitrile and Benzonitrile via Pyrolysis of Polyethylene Terephthalate (PET) with Ammonia over $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ Catalysts

Lujiang Xu ^{1,2}, Xin-wen Na ¹, Le-yao Zhang ¹, Qian Dong ¹, Guo-hua Dong ¹, Yi-tong Wang ³ and Zhen Fang ^{1,*}

¹ Biomass Group, College of Engineering, Nanjing Agricultural University, 40 Dianjiangtai Road, Nanjing 210031, Jiangsu, China; lujiangxu@njau.edu.cn (L.X.); Na_Xinwen@163.com (X.-w.N.); leyaozhang1003@163.com (L.-y.Z.); dongqianbiomass@163.com (Q.D.); dong_guohua@126.com (G.-h.D.)

² Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, China

³ College of Metallurgy and Energy, North China University of Science and Technology, 21 Bohai Street, Tangshan 063210, China; wangyt@ncst.edu.cn

* Correspondence: zhenfang@njau.edu.cn; Tel.: +86-025-58606657

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Abstract: A series of $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ catalysts were synthesized for selectively producing N-containing chemicals from polyethylene terephthalate (PET) via catalytic fast pyrolysis with ammonia (CFP-A) process. During the CFP-A process, the carboxyl group in PET plastic was efficiently utilized for the selective production of terephthalonitrile and benzonitrile by controlling the catalysts and pyrolysis parameters (e.g. temperature, residence time, ammonia content). The best conditions were selected as 2% $\text{Ca}(\text{OH})_2/\gamma\text{-Al}_2\text{O}_3$ (0.8 g), 500 °C under pure ammonia with 58.3 C% terephthalonitrile yield and 92.3% selectivity in nitriles. In addition, 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ was suitable for producing benzonitrile. With catalyst dosage of 1.2 g, residence time of 1.87 s, pyrolysis temperature of 650 °C and pure ammonia (160 mL/min carrier gas flow rate), the yield and selectivity of benzonitrile were 30.4 C% and 82.6%, respectively. The catalysts deactivated slightly after 4 cycles.

Keywords: benzonitrile; terephthalonitrile; polyethylene terephthalate (PET); catalytic pyrolysis; ammonia; $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$

1. Introduction

With the rapid development of society and the improvement of people's quality of life, more and more petroleum-based plastics are being consumed to meet people's life needs [1]. Due to its advantages of anti-acid, stability and safety, polyethylene terephthalate (PET) has been widely used as bottle materials, fibers, films, sheets, households and carpet [2]. The worldwide consumption of PET plastic was 60 million tons in 2011 and keeps growing year by year [3]. However, the high stable properties of PET make it difficult to degrade naturally and causes serious environmental problems [4,5]. Thus, the recycling of PET plastics has become urgent [6].

Catalytic fast pyrolysis (CFP) is a promising technology to convert plastics, biomass and other organic wastes to high quality bio-oil or targeted compounds within a few seconds with the help of catalyst [7–9]. Currently, different plastics (e.g. high-density polyethylene, polyvinyl chloride, polypropylene, PET, and polystyrene, etc.) are recycled efficiently by the catalytic pyrolysis process [10]. In addition, numerous kinds of reactors (e.g., batch, semi-batch, fixed bed, fluidized bed, conical spouted

bed and microwave-assisted reactors, etc.) were designed for waste plastics recycling [11,12]. Studies on catalytic pyrolysis of PET plastic were mainly carried out under inert atmosphere, and benzene-rich bio-oil was the main pyrolytic product. Yoshioka et al. [13] screened $\text{Ca}(\text{OH})_2$, NiO, TiO_2 and Fe_2O_3 on the catalytic fast pyrolysis of PET under inert atmosphere, and found $\text{Ca}(\text{OH})_2$ showed best decarboxylation performance, the yield of benzene-rich bio-oil reached 31% at 700 °C. Besides $\text{Ca}(\text{OH})_2$, CaO and zeolites (HZSM-5) also showed good catalytic performance to produce benzene-rich bio-oil. Kumagai et al. used the tandem micro (μ)-reactor-gas chromatography/mass spectrometry (TR-GC/MS) system to investigate the CaO catalytic pyrolysis of the PET process and elucidated the relationship between CaO deterioration and the aromatic hydrocarbon selectivity, and the nature of PET catalytic pyrolysis process [14,15]. Du et al. [16] used ZSM-5 zeolite and CaO to catalyze PET via pyrolysis for producing benzene-rich oil. Both catalysts showed good performance on the deoxygenation of pyrolysis products, and CaO presented better performance than ZSM-5. In addition, Xue et al. [17] used HZSM-5 to catalyze PET via pyrolysis for producing benzene-rich oil, elucidated the effect of HZSM-5 and the PET contact mode, and found that in situ catalytic pyrolysis produced more coke and aromatics than ex situ catalytic pyrolysis. Besides the benzene-rich bio-oil, benzoic acid could also be selectively produced from PET via catalytic pyrolysis over sulphated zirconia catalysts [18].

In order to make full use of the oxygen-containing functional groups in biomass and other oxygen-containing wastes, catalytic pyrolysis under ammonia process was proposed to selectively converted biomass and oxygen plastic to produce N-containing chemicals [19]. Different than the traditional pyrolysis process, the CFP-A process consisted of pyrolysis and ammonization, and ammonia was introduced as a reagent and nitrogen source. N-containing chemicals (e.g. acetonitrile, pyrrole, pyridines, indoles, and anilines) could be selectively produced from cellulose, bio-derived furans, glycerol, polylactic acid and lignin via catalytic pyrolysis with the ammonia process [20–24]. The carboxyl group in PET was not used effectively, which could be converted to amides, amines, nitriles, ketones and other value-added compounds by suitable processes.

Aromatic nitriles (e.g., terephthalonitrile, benzonitrile) have been widely applied to pharmaceuticals, pesticides, dyes and polymers [25–27]. Terephthalonitrile is a high value-added fine chemical with a price reaching over \$ 6000 per ton. It can be converted to *p*-phenylenediamine (raw material of epoxy resin and polyurethane), terephthalic acid (monomer of PET), pyrethroids pesticide, terephthalonitrile-derived nitrogen-rich network (supercapacitors), polyamidines polymers (light sensitive material) [28–30]. Benzonitrile has been widely used as solvent in the synthesis of nitrile-based rubber, resin, polymer and coatings [31–33]. It also has been used as building block for the synthesis of agrochemicals and pharmaceuticals [34,35]. The price of benzonitrile is more than \$ 4000 per ton, with over 10 thousand tons of benzonitrile being produced per year. Currently, terephthalonitrile and benzonitrile are produced by the ammoxidation of *p*-xylene, toluene industrially [36,37]. In industry, toluene is produced by the catalytic reforming gasoline or benzene alkylation reaction. *p*-Xylene is produced by separation from fossil fuel or alkyl transfer reactions of toluene [38]. However, *p*-xylene and toluene are mainly derived from non-renewable fossil-based resources. Therefore, finding a renewable or environment friendly feedstock to produce terephthalonitrile and benzonitrile is highly desirable for the green production of aromatic nitriles.

In this work, the carboxyl group in PET was utilized efficiently via pyrolysis with synthesized $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ catalysts. Terephthalonitrile and benzonitrile could be selectively produced from PET by controlling the catalysts and pyrolysis parameters in a fixed bed reactor. The parameters (pyrolysis temperature, $\text{Ca}(\text{OH})_2$ loading, catalyst usage, ammonia usage, etc), which affected the production of terephthalonitrile and benzonitrile, were investigated systematically. Furthermore, the possible reaction pathways from PET to different aromatic nitriles were investigated. Finally, catalysts stability was also studied by 4 cycle experiments. The fresh and reused catalysts were characterized by X-Ray Diffraction (XRD), N_2 adsorption/desorption, temperature programmed desorption of ammonia (NH_3 -TPD) and temperature programmed desorption of carbon dioxide (CO_2 -TPD) analyses.

2. Results and Discussions

2.1. Effect of Pyrolysis Temperature

The effect of temperature (500–700 °C) on the aromatic nitriles was investigated by using 2% $\text{Ca}(\text{OH})_2\text{-Al}_2\text{O}_3$ (1 g) at a constant flow rate of 160 mL/min carrier gas (50% ammonia and 50% nitrogen). Figure 1 shows the effect of temperature on overall yield of products and nitriles selectivity. Nitriles (the main product) and aromatics were collected by a cold trap. As temperature increased from 500 to 700 °C, the carbon yields of char, gases, nitriles and aromatics, and nitriles selectivity changed significantly. In Figure 1a, the carbon yield of char decreased from 15.85 C% at 500 °C to 6.03 C% at 700 °C, while the carbon yield of gases increased from 11.78 C% at 500 °C to 36.04 C% at 700 °C. In addition, the variation trend of nitriles carbon yield with temperature was consistent with that of char, and aromatics with that of gases. With the temperature increasing from 500 to 700 °C, the carbon yield of nitriles decreased from 53.98 to 20.61 C%. Meanwhile, the carbon yield of aromatics increased from 1.78 C% to 16.46 C%. Figure 1b shows the variation trends of different nitriles selectivity vs. temperature and the selectivity of other nitriles was very low (less than 3%). Nevertheless, the variation trends of terephthalonitrile and benzonitrile were completely opposite with the increase of temperature. At 500 °C, the selectivity of terephthalonitrile and benzonitrile was 88.88% and 8.43%, respectively. However, at 700 °C, the selectivity of terephthalonitrile decreased to 7.91%, and the selectivity of benzonitrile was up to 92.09%. Higher temperature would promote the cracking and decarboxylation reactions. Pyrolytic temperature affected the production of terephthalonitrile and benzonitrile significantly. Together with Figure 1a, the carbon yield of terephthalonitrile obtained at 500 °C reached 47.98 C%, and the carbon yield of benzonitrile obtained at 700 °C was 18.98 C%. At 650 °C, the carbon yield of benzonitrile was 24.53 C%, the highest carbon from 500–700 °C with the selectivity of benzonitrile in nitriles above 70%. Therefore, 500 °C and 650 °C were the optimal pyrolysis temperatures for selectively producing terephthalonitrile and benzonitrile. In the following tests, the effects of catalyst, residence time (between pyrolytic vapors and catalyst) and ammonia fraction in the carrier gas on the production of terephthalonitrile and benzonitrile were investigated at 500 °C and 650 °C, respectively.

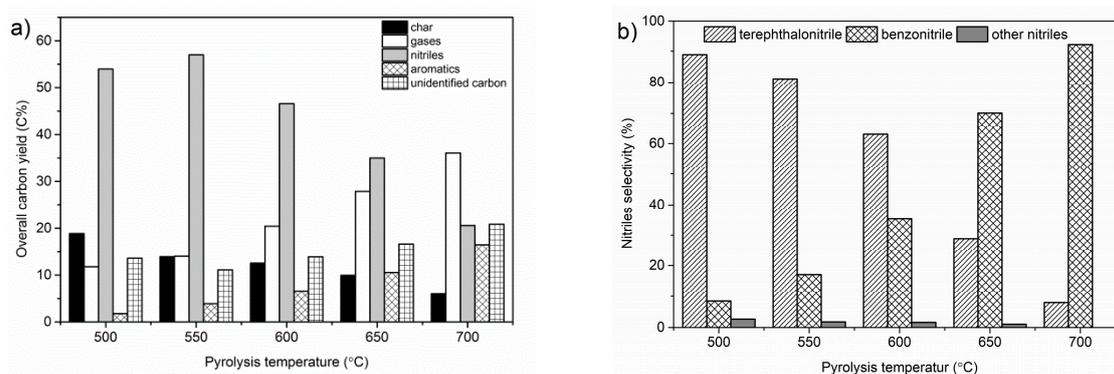


Figure 1. Effect of temperature on (a) overall yield and (b) nitriles selectivity (2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ (1 g); 80 mL/min N_2 and NH_3 flow rate, 0.5 g polyethylene terephthalate (PET) /batch).

2.2. Optimizing Conditions for Producing Terephthalonitrile at 500 °C

The effects of catalyst, residence time and ammonia content in the carrier gas on the production of terephthalonitrile were studied at 500 °C. Figure 2 shows the effect of $\text{Ca}(\text{OH})_2$ loading on $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ catalysts. Tables 1 and 2 give the effects of residence time and ammonia content, respectively.

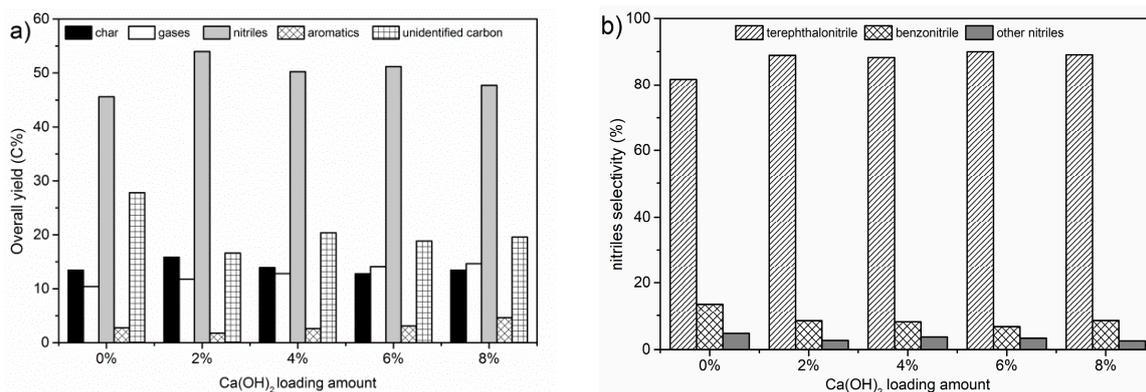


Figure 2. Effect of $\text{Ca}(\text{OH})_2$ loading on $\text{Ca}(\text{OH})_2\text{-Al}_2\text{O}_3$ catalysts on (a) overall yield and (b) nitriles selectivity for selectively producing terephthalonitrile via the catalytic fast pyrolysis of PET with ammonia at 500 °C. (1 g catalyst; N_2 and NH_3 flow rate, 80 mL/min; 0.5 g/batch PET feeding).

Table 1. Effect of residence time between pyrolytic vapors and catalyst.¹

Entry	Catalyst Dosage (g)	Residence Time (s)	Nitriles (C%)	Aromatics ² (C%)	Nitriles Selectivity (%)		
					Terephthalonitrile	Benzonitrile	Other Nitriles ³
1	0.6	0.94	57.05	1.44	90.48	6.60	2.52
2	0.8	1.25	60.53	1.51	89.91	6.81	3.29
3	1	1.56	53.98	1.78	88.88	8.43	2.69
4	1.2	1.87	54.96	3.83	86.43	8.26	5.31
5	1.5	2.34	54.52	4.69	82.89	11.48	5.63

¹ Reaction conditions: Pyrolysis temperature 500 °C; catalyst 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$; N_2 and NH_3 flow rate, 80 mL/min; PET feeding at 0.5 g/batch;. ² Aromatics: Benzene, toluene, xylenes, etc.; ³ Other nitriles: Acetonitrile, alkyl aromatic nitriles, etc.

Table 2. Effect of ammonia content in the carrier gas on selectively producing terephthalonitrile.¹

Entry	Ammonia Content (%)	Nitriles (C%)	Aromatics ² (C%)	Nitriles Selectivity (%)		
				Terephthalonitrile	Benzonitrile	Other Nitriles ³
1	25%	55.93	2.08	88.78	7.34	3.88
2	50%	60.53	1.51	89.90	6.81	3.29
3	75%	62.93	1.49	89.51	6.63	3.86
4	100%	63.18	1.73	92.28	4.11	3.61

¹ Reaction conditions: Pyrolysis temperature 500 °C; catalyst 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$; catalyst usage 0.8 g; flow rate of carrier gas: 160 mL/min; PET feeding at 0.5 g/batch;. ² Aromatics: Benzene, toluene, xylenes, etc.; ³ Other nitriles: Acetonitrile, alkyl aromatic nitriles, etc.

2.2.1. Effect of Catalyst

The effect of catalyst on selectively producing terephthalonitrile by changing $\text{Ca}(\text{OH})_2$ loading on Al_2O_3 at the range of 0–8% at 500 °C was studied with catalyst dosage and flow rate of carrier gas fixed at 1 g and 160 mL/min, as well as ammonia content in carrier gas of 50%. The effect of $\text{Ca}(\text{OH})_2$ loading on Al_2O_3 affected the nitriles and terephthalonitrile production obviously (Figure 2). In Figure 1a, the carbon yield of char, gases and aromatics changed slightly with $\text{Ca}(\text{OH})_2$ increasing from 0–8.0%, and kept around 14 C%, 12 C% and 3%, respectively. When Al_2O_3 served as catalyst, less nitriles and more unidentified compounds were produced with yields of 45.61 C% and 27.80 C%, respectively. The unidentified compounds were much more than those catalyzed by $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ catalysts. At 2% $\text{Ca}(\text{OH})_2$ loading, nitriles reached the highest yield of 53.98 C% and decreased with $\text{Ca}(\text{OH})_2$ loading increasing. At 8% $\text{Ca}(\text{OH})_2$ loading, the carbon yield of nitriles decreased to 47.69 C%. In Figure 2b, the selectivity of other nitriles was very low (around 3%). The lowest selectivity of terephthalonitrile (81.71%) and the highest selectivity of benzonitrile (13.53%) in nitriles were obtained by using neat Al_2O_3 . The highest selectivity of terephthalonitrile was 90.0% by using 6% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$. However, combined with Figure 2a, the carbon yield of terephthalonitrile was only 45.05%, which was less than that (47.98%) with 6% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$. Meanwhile, the terephthalonitrile selectivity in nitriles in the presence of 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ was 88.9%, which was slightly less than

that (90.0%) with 6% Ca(OH)₂/Al₂O₃. Therefore, 2% Ca(OH)₂ was selected as the optimal loading for producing terephthalonitrile in the following tests.

2.2.2. Effect of Residence Time Between the Pyrolytic Vapors and Catalyst

Besides temperature and catalyst, residence time between the pyrolytic vapor and catalyst also influenced the product distributions. Herein, the effect of catalyst dosage was investigated through changing catalyst dosage (from 0.6 to 1.5 g) in the presence of 2% Ca(OH)₂/Al₂O₃ at 500 °C and flowing carrier gas (50% ammonia and 50% nitrogen) at 160 mL/min. Table 2 shows that residence time and catalyst also affected the terephthalonitrile production. When catalyst dosage was 0.8 g and residence time was 1.25 s, the carbon yields of nitriles and terephthalonitrile were the highest of 60.53 C% and 54.42%, respectively. If residence time was extended further, the carbon yield of nitriles and terephthalonitrile decreased. Longer contacting time between pyrolytic vapor and catalyst would promote adequate decarboxylation and alkylation reactions during CFP-A process. At 2.34 s, the carbon yield of nitriles and terephthalonitrile was only 54.52 C% and 45.19 C%, respectively. In addition, the selectivity of terephthalonitrile in nitriles also decreased with the increase of residence time from above 90% at 0.94 s to 82.9% at 2.34 s, respectively. While, the selectivity of benzonitrile and other nitriles increased from 6.60% and 2.52% at 0.94 s to 11.48% and 5.63% at 2.34 s, respectively. By comprehensively considering the carbon yield and selectivity of terephthalonitrile, 1.25 s was the optimal residence time for selective producing terephthalonitrile, and catalyst dosage was selected as 0.8 g in the following tests.

2.2.3. Effect of Ammonia Content in the Carrier Gas

Besides decomposition reactions, ammonolysis reaction also occurred. Ammonia acted both as carrier gas and reactant for producing nitriles, and is as important as PET and catalyst in this process. The effect of NH₃ content (from 25% to 100%) in the carrier gas was investigated by fixing pyrolysis temperature (500 °C), catalyst dosage (2% Ca(OH)₂/Al₂O₃, 0.8 g), and carrier gas flow rate (160 mL/min). In Table 3, the higher ammonia content yielded more nitriles and terephthalonitrile. As ammonia content increased from 25% to 100%, the carbon yield of nitriles and terephthalonitrile increased from 55.93 C% and 49.66 C% to 63.18 C% and 58.30 C%, respectively. Meanwhile, the selectivity of terephthalonitrile in nitriles also increased from 88.78% (25% NH₃) to 92.28% (100% NH₃). Therefore, as compared with the mixture of N₂ and NH₃, pure ammonia was more suitable and used as carrier gas in the terephthalonitrile production process. The best conditions for the production of terephthalonitrile are selected as 0.8 g of 2% Ca(OH)₂/γ-Al₂O₃, 500 °C under pure ammonia with 58.30 C% terephthalonitrile yield and 92.28% selectivity in nitriles.

Table 3. Effect of residence time between pyrolytic vapors and catalyst.¹

Entry	Catalyst Dosage (g)	Residence Time (s)	Nitriles (C%)	Aromatics ² (C%)	Nitriles Selectivity (%)		
					Terephthalonitrile	Benzonitrile	Other Nitriles ³
1	0.6	0.94	32.93	6.33	28.36	64.74	6.89
2	0.8	1.25	31.14	7.85	15.35	77.91	6.74
3	1	1.56	33.1	10.11	12.36	81.12	6.53
4	1.2	1.87	32.96	13.94	6.43	84.98	8.59
5	1.5	2.34	32.05	15.87	4.21	84.21	11.58

¹ Reaction conditions: Pyrolysis temperature 650 °C; catalyst 4% Ca(OH)₂/Al₂O₃; N₂ and NH₃ flow rate, 80 mL/min; PET feeding at 0.5 g/batch; ² Aromatics: Benzene, toluene, xylenes, etc.; ³ Other nitriles: Acetonitrile, alkyl aromatic nitriles, etc.

2.3. Optimizing Benzonitrile Production at 650 °C

Similarly, the effects of catalyst, residence time and ammonia content on the production of benzonitrile were studied at 650 °C. Figure 3 shows the effect of Ca(OH)₂ loading of Ca(OH)₂/Al₂O₃ catalysts, Tables 4 and 5 give the effect of residence time and effect of ammonia content in the carrier gas on the production of benzonitrile.

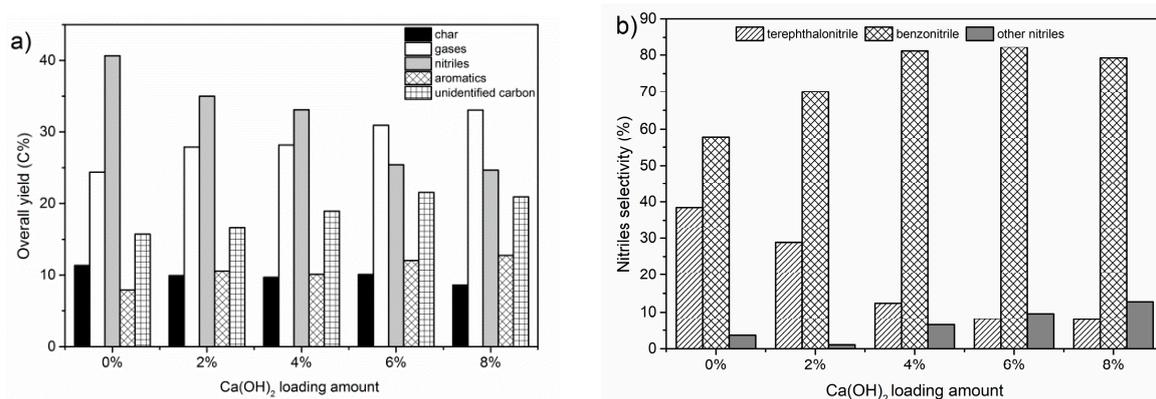


Figure 3. Effect of Ca(OH)₂ loading on Ca(OH)₂-Al₂O₃ catalysts on (a) overall yield and (b) nitriles selectivity for selectively producing terephthalonitrile via the catalytic fast pyrolysis of PET with ammonia at 650 °C. (1 g catalyst; N₂ and NH₃ flow rate, 80 mL/min; PET feeding, 0.5 g/batch)

Table 4. Effect of ammonia content in the carrier gas on selectively producing benzonitrile.¹

Entry	Ammonia Content (%)	Nitriles (C%)	Aromatics ² (C%)	Nitriles Selectivity (%)		
				Terephthalonitrile	Benzonitrile	Other Nitriles ³
1	25%	25.53	15.81	7.46	84.04	8.5
2	50%	32.96	13.94	6.43	84.98	8.59
3	75%	34.14	13.5	6.85	84.33	8.82
4	100%	36.83	12.56	8.12	82.60	9.28

¹ Reaction conditions: Pyrolysis temperature 650 °C; catalyst: 4% Ca(OH)₂/Al₂O₃; catalyst usage 1.2 g; flow rate of carrier gas: 160 mL/min; PET feeding at 0.5 g/batch;. ² Aromatics: Benzene, toluene, xylenes, etc.; ³ Other nitriles: Acetonitrile, alkyl aromatic nitriles, etc.

Table 5. Summary of catalytic fast pyrolysis with ammonia (CFP-A) of model chemicals over 4% Ca(OH)₂/Al₂O₃ at 650 °C.¹

Entry	Feedstock	Nitriles (C%)	Aromatics ² (C%)	Nitriles Selectivity (%)		
				Terephthalonitrile	Benzonitrile	Other Nitriles ³
1	Benzoic acid	68.75	3.02	N.D	100	N.D
2	Methyl benzoate	64.34	3.46	N.D	98.78	1.22
3	Benzamide	86.56	5.68	N.D	100	N.D
4	Terephthalic acid	56.05	2.89	53.02	45.43	1.55
5	Dimethyl terephthalate	59.52	3.27	49.59	47.54	2.86
6	Benzonitrile	95.74	0.45	N.D	100	N.D

¹ Reaction conditions: Pyrolysis temperature 650 °C; catalyst: 4% Ca(OH)₂/Al₂O₃; catalyst usage 1.2 g; flow rate of carrier gas: 160 mL/min; PET feeding at 0.5 g/batch;. ² Aromatics: Benzene, toluene, xylenes, etc.; ³ Other nitriles: Acetonitrile, alkyl aromatic nitriles, etc.

2.3.1. Effect of Catalyst

The effect of Ca(OH)₂ loading on Al₂O₃ on selectively producing benzonitrile was investigated. The Ca(OH)₂ loading on Al₂O₃ was in the range of 0–8%. Compared to the production of terephthalonitrile, Ca(OH)₂ loading on Al₂O₃ had a more obvious influence (especially on the catalytic cracking and decarboxylation) on the producing benzonitrile. In Figure 3a, the more Ca(OH)₂ loading on Al₂O₃, the more gases, aromatics and unidentified carbon were produced with less nitriles. When 8% Ca(OH)₂/Al₂O₃ served as catalyst, the carbon yield of nitriles was only 24.67 C%, much less than that (40.65 C%) with neat Al₂O₃. Figure 3b shows that Ca(OH)₂ loading on Al₂O₃ could promote the formation of benzonitrile but inhibit terephthalonitrile production. In the presence of 6% Ca(OH)₂/Al₂O₃, the highest selectivity of benzonitrile in nitriles (82.24%) was obtained. In addition, the selectivity of benzonitrile with 4% Ca(OH)₂/Al₂O₃ was 81.12 %, which was similar to that of 6% Ca(OH)₂/Al₂O₃. Therefore, 4% Ca(OH)₂/Al₂O₃ was selected for producing benzonitrile in the following tests.

2.3.2. Effect of Residence Time

The effect of residence time on benzonitrile production was studied by changing catalyst (4% Ca(OH)₂/Al₂O₃) dosage (from 0.6 to 1.5 g) at 650 °C and carrier gas (50% NH₃ and 50% N₂) flow rate of 160 mL/min. In Table 2, residence time affected the carbon yield of nitriles slightly, but affected the carbon yield of aromatics and the nitriles selectivity significantly. The effect of residence time on the production of benzonitrile at 650 °C was similar to that of the production of terephthalonitrile at 500 °C. Longer residence time could promote PET to form more benzonitrile and aromatics and less terephthalonitrile. The carbon yield and selectivity of benzonitrile in nitriles were the highest of 28.01 C% and 84.98 %, respectively at residence time of 1.87 s (catalyst dosage of 1.2 g). Therefore, 1.87 s was selected as optimal residence time for producing benzonitrile with catalyst dosage of 1.2 g in the following tests.

2.3.3. Effect of Ammonia Content

The effect of NH₃ content (25% to 100%) on the production of benzonitrile was investigated by fixing temperature (650 °C), catalyst dosage (4% Ca(OH)₂/Al₂O₃, 1.2 g) and carrier gas flow rate (160 mL/min). The effect of ammonia content on benzonitrile production (Table 4) was the same as that on terephthalonitrile production (Table 3). The higher ammonia content could cause more nitriles and benzonitrile production. When pure ammonia served as carrier gas, the carbon yields of nitriles and benzonitrile were 36.83 C% and 30.42 C%, which were much higher than those (25.53 C% and 21.45%) with 25% ammonia. Meanwhile, the selectivity of benzonitrile in nitriles was up to 82.60%. Therefore, pure ammonia was more suitable and used as carrier gas in the benzonitrile production process. The optimal conditions for the production of benzonitrile were selected as 1.2 g of 4% Ca(OH)₂/γ-Al₂O₃, 650 °C under pure ammonia with 30.42 C% benzonitrile yield and 82.60% selectivity in nitriles.

2.4. Possible Reaction Pathways from PET to Terephthalonitrile and Benzonitrile

The reaction pathways from PET to terephthalonitrile were investigated in the previous study on selectively producing terephthalonitrile by CFP-A of PET over H₃PO₄ modified Al₂O₃ catalysts at 500 °C [39]. Terephthalic acid and related esters were the key intermediates for the production of terephthalonitrile from PET. Herein, the possible reaction pathways from PET to benzonitrile at 650 °C were also investigated by a series of experiments. Firstly, the pyrolysis experiment of PET without catalyst under ammonia was carried out. The detailed product distributions were detected by GC-MS (Agilent 7890-5977B, Santa Clara, CA; Figure S1 and Table S1 in Supplementary Materials). The pyrolytic products were benzoic acid and its derived esters, benzamide, terephthalic acid and its derived esters. Therefore, benzoic acid, methyl benzoate, benzamide, terephthalic acid, dimethyl terephthalate and benzonitrile were employed as the feedstocks for producing nitriles (Table 5). In entries 1–3, benzoic acid, benzamide and methyl benzoate could be easily converted to benzonitrile with high selectivity (> 98%) through the acid-catalyzed ammoniation and dehydration reactions over Al₂O₃-based catalysts. It indicated that benzoic acid, benzamide, methyl benzoate were the key intermediates from PET to benzonitrile. In addition, as terephthalic acid and dimethyl terephthalate served as feedstocks (entries 4 and 5), the main product was terephthalonitrile and benzonitrile. The selectivity of benzonitrile in nitriles was more than 45%. The results showed that benzonitrile could be produced from terephthalic acid and dimethyl terephthalate at higher pyrolysis temperature via selective decarboxylation reaction over Ca(OH)₂/γ-Al₂O₃ catalyst.

Besides the nitriles, a certain amount of aromatic hydrocarbons could also be detected. Under the optimal conditions for producing benzonitrile, the carbon yield of aromatics was around 13 C%. Under the same conditions, the carbon yields of model compounds were less than 6%, and more aromatics were produced from benzamide than those of aromatic acids and their derived esters. Meanwhile, as benzonitrile served as feedstocks, less than 1% of aromatics were detected in the products.

It indicated that aromatics could not be produced by the further cracking of benzonitrile, and benzonitrile was stable during the CFP-A process. The carbon-carbon bond dissociation energy of model compounds (Table S2) was calculated based on the DFT method with much weaker value for benzamide than those of nitriles, and aromatic acids and their derived esters. Aromatics (e.g., toluene, styrene, biphenyl) were detected during the thermal decomposition of PET without catalyst. Therefore, aromatics could be produced from PET by the direct thermal decomposition process, they could also be produced from benzamide, aromatic acids and derived esters via catalytic decarboxylation and cracking reactions over $\text{Ca}(\text{OH})_2/\gamma\text{-Al}_2\text{O}_3$ catalyst during the CFP-A process.

Based on all the above findings, the reaction pathways from PET to terephthalonitrile and benzonitrile were proposed and summarized in Figure 4. At lower temperature (500 °C), terephthalic acid and its derived esters were the main pyrolytic products, and the key intermediates from PET to terephthalonitrile. At a higher temperature (650 °C), benzoic acid, methyl benzoate, benzamide were the main intermediates from PET to benzonitrile. Aromatics were produced as by-products from PET, benzamide, aromatic acids and derived esters via thermal decomposition, decarbonylation, cracking reaction during the CFP-A process.

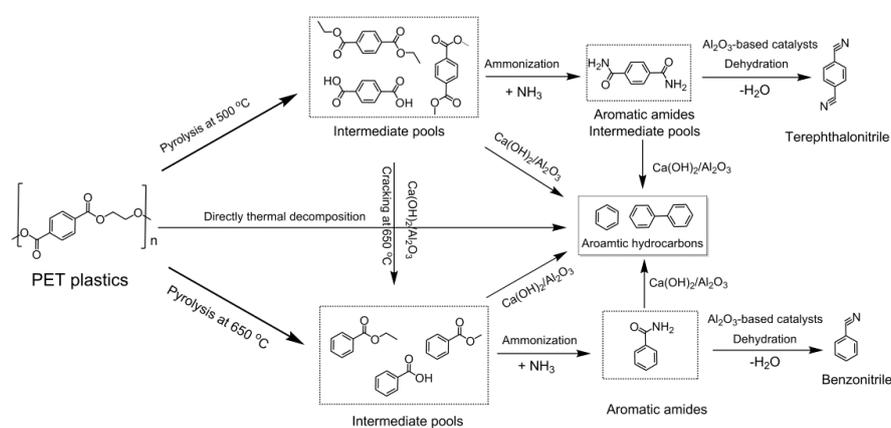


Figure 4. Possible reaction pathways from PET to terephthalonitrile and benzonitrile.

2.5. Catalysts Stability

The stability of catalysts was studied by conducting 4 reaction/regeneration cycles at the optimal conditions for terephthalonitrile and benzonitrile. BET (Barrett–Emmet–Taller) surface area, pore volume, acidity and basicity were also investigated to illustrate the deactivation of catalysts. For each cycle, the spent catalyst was calcined with air (100 mL/min) at 650 °C for 3 h to remove the coke formed on the surface of the catalyst. In Figure 5a, as compared to the fresh catalyst, the carbon yield of nitriles and terephthalonitrile did not decrease after 2 cycles, indicating that the catalyst (2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$) kept stable for the first and second cycles. After 4 cycles, the carbon yield of nitriles and terephthalonitrile decreased to 60.62 C% and 54.76 C%, slightly decreased by 6% as compared to that at the first cycle (63.17 C% and 58.30 C%). In Figure 5b, 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ deactivated little at the first and second cycles for producing benzonitrile. However, after 4 cycles, the carbon yield of nitriles and benzonitrile decreased to 34.49% and 25.18%, respectively. Therefore, the above results suggested that 2% and 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ catalysts were stable for the production of terephthalonitrile and benzonitrile.

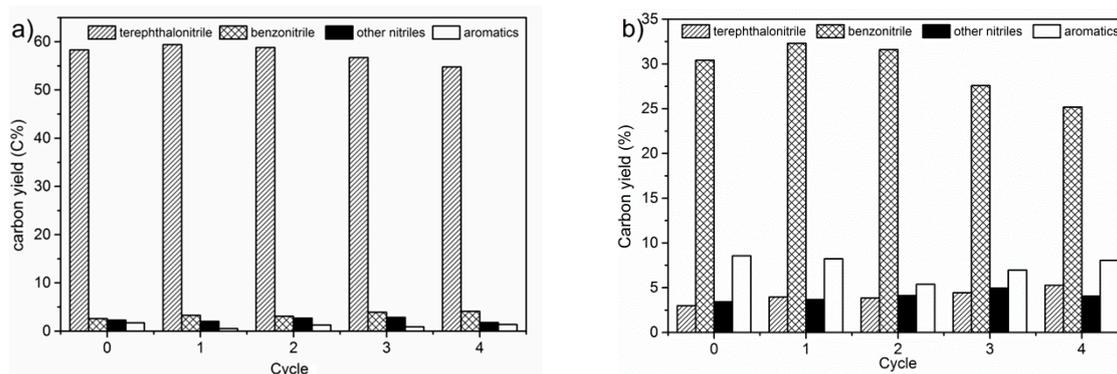


Figure 5. Yield of products vs. catalyst cycle for (a) terephthalonitrile at 500 °C, and (b) benzonitrile at 650 °C. ((a) 1g 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$; N_2 and NH_3 flow rate, 120 mL/min and 40 ml; PET feeding, 0.5 g/batch; (b) 1.2g 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$; ammonia, 160 mL/min; PET feeding, 0.5 g/batch).

2.6. Catalysts Characterization

The fresh and used catalysts after 4 cycles were characterized by XRD, N_2 adsorption/desorption, NH_3 -TPD and CO_2 -TPD. In Figure 6 for XRD patterns, the peaks at 18.5° , 20.4° , 36.8° , 27.8° and 66.7° (2θ) of fresh 2% and 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ were the characteristic ones for $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, the peaks at 37° , 46° and 66.7° of recycled catalysts were the characteristic ones for Al_2O_3 . The crystallinity of catalysts changed a lot during the reactions. In addition, no characteristic peaks of $\text{Ca}(\text{OH})_2$ and its derives were detected in Figure 6, indicating that the crystallinity of $\text{Ca}(\text{OH})_2$ was not very high and $\text{Ca}(\text{OH})_2$ was dispersed well on the surface of $\gamma\text{-Al}_2\text{O}_3$. BET surface area, pore volume, total acid amounts and total basic amounts were given in Table 6. The BET surface area and pore volume of fresh 2% and 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ were $148.14 \text{ m}^2/\text{g}$ & $0.70 \text{ cm}^3/\text{g}$, and $147.13 \text{ m}^2/\text{g}$ & $0.69 \text{ cm}^3/\text{g}$, but decreased to $116.76 \text{ m}^2/\text{g}$ & $0.56 \text{ cm}^3/\text{g}$, and $122.63 \text{ m}^2/\text{g}$ & $0.60 \text{ cm}^3/\text{g}$ after 4 cycles, respectively. It also indicated the changes of catalyst micro structure during cycles. The total acid amounts and basic amounts of fresh and used catalysts measured by NH_3 -TPD and CO_2 -TPD were summarized in Table 6 with detailed spectra given in Figures S2 and S3. As compared with 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$, 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$ has higher total acid amounts ($377.05 \mu\text{mol NH}_3/\text{g}$) and basic amounts ($241.24 \mu\text{mol CO}_2/\text{g}$). After 4 cycles for producing terephthalonitrile at 500 °C with 2% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$, the acid amounts of used catalyst decreased slightly to $295.74 \mu\text{mol NH}_3/\text{g}$, while the basic amounts decreased significantly to 77.40 from $197.54 \mu\text{mol CO}_2/\text{g}$. For 4% $\text{Ca}(\text{OH})_2/\text{Al}_2\text{O}_3$, the total acid amounts and basic amounts decreased significantly after 4 cycles at 650 °C.

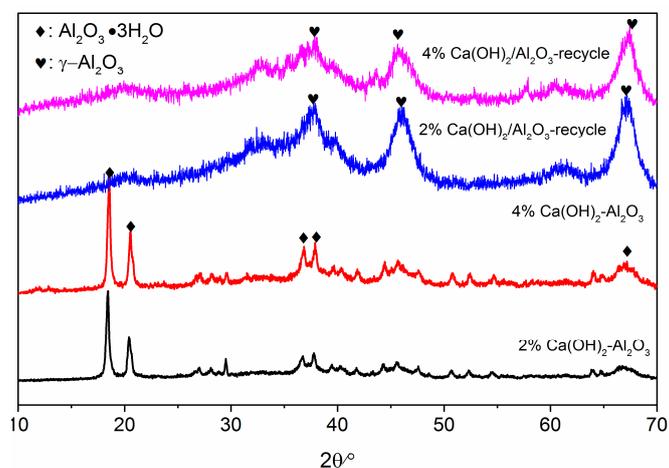


Figure 6. XRD patterns of fresh and used catalysts.

Table 6. Typical properties of catalysts.

Entry	Catalysts	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Total Acid Amounts (μmol NH ₃ /g)	Total Basic Amounts (μmol CO ₂ /g)
1	2% Ca(OH) ₂ /γ-Al ₂ O ₃	148.14	0.70	303.91	197.54
2	4% Ca(OH) ₂ /γ-Al ₂ O ₃	147.13	0.69	377.05	241.24
3	Used 2% Ca(OH) ₂ /Al ₂ O ₃ ¹	116.76	0.56	295.74	77.40
4	Used 4% Ca(OH) ₂ /Al ₂ O ₃ ²	122.63	0.60	160.58	99.16

¹ Used 2% Ca(OH)₂/Al₂O₃: After 4 cycles for producing terephthalonitrile at 500 °C and 160 mL of pure ammonia, and remove coke with air (100 mL/min) at 650 °C for 3 h. ² Used 4% Ca(OH)₂/Al₂O₃: After 4 cycles for producing benzonitrile at 650 °C and 160 mL of pure ammonia, remove coke with air (100 mL/min) at 650 °C for 3 h.

3. Materials and Methods

3.1. Materials

Methanol (≥99.5%), benzene (≥99.5%), toluene (≥99.5%), xylene (≥99.5%), biphenyl (≥99.5%) and Ca(OH)₂ (≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China. Bi-cyclohexane (≥99.5%), naphthalene (≥99.5%), terephthalonitrile (≥99.5%), benzonitrile (≥99.5%) and terephthalamide (>98%) as calibrants, benzoic acid (99%), p-phthalic acid (99%), benzamide (≥99.5%), methyl benzoate (≥99.5%), dimethyl terephthalate (≥99%) and γ-Al₂O₃ (20 nm) were purchased from Aladin Chemical Reagent Co. Ltd (Shanghai, China).

PET powder (AR, ~100 meshes) were purchased from Shanghai Youngling-Tech Co. Ltd., Shanghai, China. All these chemicals and materials were used without further purification. The elemental analysis of PET powders was shown in Table S3.

Air, NH₃ (≥99.995%, AR), N₂ (99.999%), Ar (99.999%), He (99.999%) were purchased from Nanjing Special Gases Factory, Jiangsu, China. The standard gas (C6+ 0.0920%, CH₄ 53.922%, C₂H₂ 0.561%, C₃H₄ 0.523%, trans -butane 0.501%, cis-butane 0.505%, 1,3-butadiene 0.523%, N₂ 10.40%, C₂H₄ 1.01%, C₃H₈ 1.01%, iso-butane 2.01%, n-butene 0.532%, isopentane 0.505%, CO₂ 2.02%, CO 0.986%, C₂H₆ 1.05%, C₃H₆ 1.01%, n-butane 1.98%, isobutene 0.505%, n-pentane 0.515%, O₂ 5.10%, H₂ 14.74%) was purchased from Dalian Special Gases Co., Ltd (Dalian, China) for gas calibration.

3.2. Catalysts Preparation and Regeneration

For Ca(OH)₂/γ-Al₂O₃: The modified γ-Al₂O₃ catalysts were prepared by wetness impregnation with aqueous Ca(OH)₂ solution [(mass ratio from 2% to 8% based on Ca(OH)₂ (the mass ratio of γ-Al₂O₃ to water was 1:10)]. After the impregnation, the catalysts were dried in an oven at 110 °C for 12 h, and calcined at 550 °C for 4 h in air. All the above catalysts were crushed and screened for about 40 meshes. For catalyst regeneration, after each cycle, catalyst was calcined with air (100 mL/min) at 550 °C for 3 h to remove coke.

3.3 Catalyst Characterization

Catalysts were analyzed on a theta rotating anode X-ray diffractometer (TTP-III, Rigaku, Tokyo, Japan) using CuKα radiation at 40 kV and 40 mA, with 2θ ranges of 10°–70° at scan rate of 10 °/min. The nitrogen adsorption/desorption isotherms of the catalysts were measured by Autosorb-iQ (Quantachrome, Boynton Beach, FL, USA). The surface area and total volume were determined through the BET method. The NH₃-TPD and CO₂-TPD tests of the catalyst were conducted with Chembet PULSAR temperature-programmed reduction/desorption (TPR/TPD) (Quantachrome, Boynton Beach, FL, USA). The detailed method of NH₃-TPD was referred to previous work [16]. The CO₂-TPD for acidity test of the catalyst was also conducted with the Chembet PULSAR TPR/TPD. Four different volumes (0.5, 1, 1.5, 2 mL) of a standard CO₂ gas were used to calibrate total basic density with R² > 0.999. About 200 mg of sample were put in a reactor and pre-treated in situ for 4 h at 550 °C in a flow of argon. After cooling to 100 °C, CO₂ adsorption was performed by feeding pulses of CO₂ to the reactor. After the catalyst surface became saturated, the sample was kept at 100 °C for 2 h to

remove the base excess. CO₂ was thermally desorbed by rising the temperature with a linear heating rate of approximately 10 °C/min from 100 to 500 °C.

3.3. Pyrolysis Experiments

Catalytic pyrolysis of PET was carried out in a fixed bed reactor (Anhui Kemi Machinery Technology Co. LTD, Hefei, China) at 450 to 700 °C (height: 400 mm, internal diameter: 10 mm; Figure S4). All the experiments were isothermal and batch. For each run, the catalyst was fixed in the reactor as catalyst bed, and solid PET was fed manually into the reactor under a certain rate and purged with carrier gas. The volatile products were trapped in a cold trap, and diluted with hot methanol for GC and GC/MS analysis. The non-condensable gas products were collected with a gas bag, and washed with phosphoric acid solution to remove excess ammonia. The volume of gas products was measured via drainage method, and its compositions were determined by GC. Due to p-phthalic acid, benzoic acid, benzamide, methyl benzoate, dimethyl terephthalate were the solid feedstocks, they were fed the same as PET for catalytic pyrolysis. Benzonitrile was liquid at room temperature and injected to the reactor for pyrolysis experiments. The detailed pyrolysis system was shown in Figure S5.

3.4. Products Analyses

The liquid samples were analyzed by a GC-MS (Agilent 7890B-5977B, Agilent Technologies Inc. Santa Clara, CA, USA) equipped with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 mm). Split injection was performed at a split ratio of 50 using helium (99.999%) as carrier gas. The oven temperature was held at 40 °C for 3 min, heated to 280 °C at 10 °C/min, and held at 280 °C for 5 min. The GC-MS mode was shown in Table S4.

The carbon yield and selectivity of coke, bio-oil and gases products were quantitatively determined by elemental analysis (Elementar, Langensfeld, Germany), GC. The liquid products (such as aromatic nitriles, aromatic hydrocarbons) were quantitatively determined by GC (GC-2010 plus, Shimadzu, Kyoto) employing a 30m × 0.25mm × 0.25µm fused-silica capillary column (DB-Wax, Shimadzu). The products in the cold trap were mixed with bi-cyclohexane as the internal standard with calibration factor of 1.084 for benzonitrile, 1.261 for terephthalonitrile, 0.941 for benzene, 1.023 for toluene, 1.112 for naphthalene and diluted by hot methanol (25 mL) for GC analysis. The GC operating conditions were as follows: Carrier gas—nitrogen; injection port—250 °C in a split mode; detector (FID)—250 °C; column temperature—40 °C; oven temperature program—heating up to 250 °C at a rate of 10 °C/min, and holding at a final temperature for 10.0 min.

For gas product analysis, the entire gas of each run was collected with an air bag, weighed, and analyzed using GC (GC-2014C, Shimadzu, Kyoto, Japan) with two detectors and four columns (PC1: P-N 80/100 mesh, 3.2 × 2.1 mm × 1 m; MC-1: P-N 80/100 mesh, 3.2 × 2.1 mm × 1.0 m; MC-2: MS-13X, 80/100 mesh, 3.2 × 2.1 mm × 2 m; MC-3: HP-Al₂O₃, 30 m × 0.53 mm × 15 µm), a thermal conductivity detector (TCD), PC-1, MC-1 and MC2 columns for analysis of H₂, CO, CH₄ and CO₂, and a flame ionization detector (FID) and MC-3 column for gas hydrocarbons. The moles of gas products were externally calibrated with three different concentrations diluted with N₂ from the standard gas mixture. The GC operating conditions were as follows: Carrier gas—nitrogen and argon; detector (FID and TCD)—150 °C; column temperature—50 °C; oven temperature program—holding at 50 °C for 3 min, heating up to 130 °C at a rate of 10 °C/min, and holding for 3 min. In addition, due to the excess ammonia existing in this process, which is easy to react with CO₂ (formed in the pyrolysis process), thus CO₂ couldn't be detected by GC in this study.

The carbon yield of coke, gases, nitriles, aromatics and nitriles selectivity were calculated from Equations (1) to (5) as described in previous work [29]. The unidentified carbon yield was calculated from Equation (6) by mass balance closure. The residence time was calculated from Equation (7)

$$\text{Coke yield (C\%)} = \text{Carbon moles in coke/Carbon moles in PET feeding} \times 100\% \quad (1)$$

$$\text{Gases yield (C\%)} = \text{Carbon moles in gases/Carbon moles in PET feeding} \times 100\% \quad (2)$$

$$\text{Nitriles yield (C\%)} = \text{Carbon moles in nitriles/Carbon moles in PET feeding} \times 100\% \quad (3)$$

$$\text{Aromatics yield(C\%)} = \text{Carbon moles in aromatics/Carbon moles in PET feeding} \times 100\% \quad (4)$$

$$\text{Nitriles selectivity (\%)} = \text{Carbon moles in specific nitrile/Carbon moles in all nitriles} \times 100\% \quad (5)$$

$$\text{Unidentified carbon yield (C \%)} = 100\% - \text{identified carbon yield} \quad (6)$$

$$\text{Residence time (s)} = \text{Catalyst volume/Carrier gas flow rate} \quad (7)$$

4. Conclusions

Ca(OH)₂/Al₂O₃ catalysts were used to produce terephthalonitrile and benzonitrile from polyethylene terephthalate (PET) via catalytic fast pyrolysis with the ammonia process. The best conditions for the production of terephthalonitrile were selected as 0.8 g of 2% Ca(OH)₂/γ-Al₂O₃, 500 °C under pure ammonia with 58.30 C% terephthalonitrile yield and 92.28% selectivity in nitriles. In addition, 4% Ca(OH)₂/Al₂O₃ was the suitable catalyst for producing benzonitrile. Under conditions with catalyst dosage of 1.2 g, residence time of 1.87 s at 650 °C and pure ammonia flowing of 160 mL/min, the yield and selectivity of benzonitrile was 30.42 C% and 82.60%, respectively. After 4 cycles, the catalysts deactivated slightly and kept stable. The fresh and used catalysts were further characterized with XRD, N₂ adsorption/desorption, NH₃-TPD and CO₂-TPD.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/5/436/s1>, Figure S1. The GC-MS spectra of pyrolysis PET with ammonia at 650 °C; Figure S2. The NH₃-TPD spectra of fresh and used catalysts; Figure S3. The CO₂-TPD spectra of fresh and used catalysts; Figure S4. The schematic diagram of the pyrolysis system; Figure S5. The schematic diagram of the liquid feeding pyrolysis system; Table S1. The detailed chemical compositions of pyrolysis PET with ammonia at 650 °C; Table S2. C-C Bond dissociation energy of some model compounds @25 °C and @650 °C; Table S3. Elemental analyses of PET plastic; Table S4. Integration parameters and their values set in mass spectrometry detector (MSD) ChemStation.

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Conflicts of Interest: There are no conflicts to declare.

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