A New Strategy for the Preparation of Terephthalic Acid by the Aerobic Oxidation of *p*-Xylene Using *N*-Hydroxyphthalimide as a Catalyst

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Abstract: A new methodology for the production of terephthalic acid (**3**) by the aerobic oxidation of *p*-xylene (**1**) using a combined catalytic system of *N*-hydroxyphthalimide (NHPI)/$Co(OAc)_2$/$Mn(OAc)_2$ was developed. The oxidation of **1** under a dioxygen atmosphere in the presence of a catalytic amount of NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ at 100 °C for 14 h afforded terephthalic acid in 82% yield. Removal of $Mn(OAc)_2$ from the catalytic system resulted in considerable reduction in the yield of **3**. When the oxidation of **1** was carried out under a pressure of air (30 atm) at 150 °C, the reaction was completed within 3 h to give **3** in 84% yield. The oxidation of *p*-toluic acid (**2**), which can be prepared by the oxidation of **1** using the NHPI/$Co(OAc)_2$ system at room temperature, by the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system under pressure of air (30 atm) at 150 °C gave **3** in 95% yield. *N*-Acetoxyphthalimide (NAPI) was found to require a lower catalyst loading than NHPI, but oxidation with NAPI was slower. Thus, the oxidation of **1** catalyzed by NAPI (5 mol %)/$Co(OAc)_2$ (0.5 mol %)/$Mn(OAc)_2$ (0.5 mol %) under a dioxygen atmosphere (1 atm) in acetic acid at 100 °C gave **3** in 80% yield.

Introduction

Direct oxidation of hydrocarbons with air (O_2) is a commercially important reaction for the production of oxygen-containing compounds such as alcohols, ketones and carboxylic acids from petroleum feedstock and natural gas.[1] Among the carboxylic acids manufactured by the oxidation of hydrocarbons, terephthalic acid (TPA) derived from *p*-xylene has recently become an important, fast-growing chemical as a raw material for polyethylene terephthalate (PET).[2] In 1999, ca. 26 million tons of PET were manufactured worldwide and its growth is estimated at a minimum of 5% annually to the year 2002.

Nowadays, about 70% of the TPA used worldwide is produced by the catalytic oxidation of *p*-xylene discovered by Scientific Design and Amoco.[2,3] The oxidation is catalyzed by a mixture of heavy metals, most commonly cobalt and manganese salts, and bromine, typically in the form of HBr, NaBr, or tetrabromoethane. In the conventional process, the reactor is maintained at an operating temperature between 175–225 °C and pressure between 15–30 atm of air, using acetic acid as a solvent. Because corrosive bromine is used, vessels lined with titanium or other expensive metals are necessary. The crude TPA produced is unsuitable as a feedstock for polyester, primarily owing to the 4-carboxybenzaldehyde (4-CBA) formed as a side product which acts as a chain terminator in polymerization reactions that convert PTA to its most important end products, polyester fibers and PET resins. In order to obtain pure TPA in a fiber grade, a purification process has jointly been developed by Scientific Design and Amoco, in which the 4-CBA is hydrogenated to *p*-toluic acid by hydrogen with a carbon-supported palladium catalyst.[2,4] Thus, PTA including less than 25 ppm of 4-CBA is now produced.

Until the development of the Amoco purification process of TPA, only dimethyl terephthalate (DMT) was used as a raw material for PET production, since DMT could be purified to the fiber grade by crystallization.[2] DMT is manufactured through the following four steps developed by C. W. Witten and modified by Hercules and Dynamit-Nobel. First, *p*-xylene is oxidized to *p*-toluic acid. It then passes to an esterification step to form methyl *p*-toluate. The methyl *p*-toluate is isolated and returned to the oxidation reactor,

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giving monomethyl terephthalate, followed by esterification to DMT.

Since the Amoco purification process for TPA was developed, almost all of the new plants use the Amoco oxidation process. This process, however, has some disadvantages: i. e., the use of bromine as a promoter which corrodes the reactor, and the requirement of a high operating temperature. From economical and environmental points of view, the development of a new oxidation system, which overcomes these disadvantages for the production of PTA, is desired.

In our preceding papers, we showed that *N*-hydroxyphthalimide (NHPI) promotes the oxidation of a variety of hydrocarbons with dioxygen in the presence or absence of transition metal salts.[5] In this oxidation, the phthalimide *N*-oxyl radical (PINO) generated *in situ* from the NHPI and dioxygen abstracts the hydrogen atom from the hydrocarbon to form an alkyl radical, which is readily trapped by dioxygen, affording oxygenated-compounds. Thus, the aerobic oxidation of toluene to benzoic acid under normal pressure and temperature (1 atm, 25 °C) has first been achieved in high yield (81%) through a catalytic process using NHPI combined with $Co(OAc)_2$.[5b] In this paper, we wish to report a new strategy for the production of PTA by the NHPI-catalyzed aerobic oxidation of *p*-xylene under halogen-free conditions.

Results and Discussion

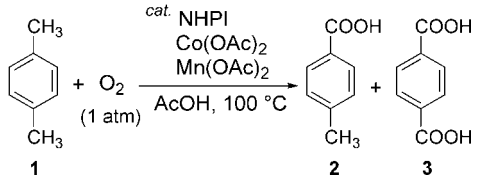
Direct Oxidation of *p*-Xylene to Terephthalic Acid (TPA)

The oxidation of *p*-xylene (**1**) with molecular oxygen (1 atm) in the presence of a catalytic amount of NHPI (20 mol %), $Co(OAc)_2$ (0.5 mol %), and $Mn(OAc)_2$ (0.5 mol %) using acetic acid as solvent at 100 °C for 14 h afforded terephthalic acid (**3**) in 82% yield and *p*-toluic acid (**2**) (4% yield) together with small amounts of 4-carboxybenzaldehyde (4-CBA), 4-carboxybenzyl alcohol, 1,4-diacetoxymethylbenzene, and 4-acetoxymethylbenzoic acid as well as several unidentified species in 1–2% yields, respectively, at >99% conversion (Scheme 1, Table 1, run 4). Table 1 summarizes representative results for the oxidation of **1** with dioxygen (1 atm) under various reaction conditions. The oxidation of **1** by NHPI alone gave **2** in low yield (12%) and low conversion (14%) of **1**, but **3** was not formed at all (run 1). Substrate **1** was converted into **3** in 67% yield by the use of NHPI combined with $Co(OAc)_2$, while the same oxidation by NHPI combined with $Mn(OAc)_2$ led to **2** rather than **3** as a major product (runs 2 and 3). Since the synergistic effect of Co and Mn salts in the aerobic oxidation of hydrocarbons such as *p*-xylene has been reported,[6] the NHPI catalyst combined with $Co(OAc)_2$ and $Mn(OAc)_2$ was employed. The yield of **3** was considerably dependent on the amount of NHPI used (runs 5 and 6). The oxidation at 90 °C afforded **3** in slightly lower yield (73%) (run 8). Several solvents were examined in the present oxidation. Among them, acetic acid, commonly used in the industrial oxidation of these substrates, was found to be the best solvent (runs 9 and 10). Needless to say, almost no reaction took place in the absence of NHPI under these conditions (run 11).

Table 1. Oxidation of *p*-xylene (**1**) catalyzed by NHPI[a]

Run	Catalyst (mol %)			Yield (%)	
	NHPI	$Co(OAc)_2$	$Mn(OAc)_2$	**2**	**3**
1	20	–	–	12	n. d.
2	20	0.5	–	15	67
3	20	–	0.5	54	6
4[b]	20	0.5	0.5	4	82
5	15	0.5	0.5	31	48
6	10	0.5	0.5	72	21
7[c]	10	0.5	0.5	31	55
8[d]	20	0.5	0.5	13	73
9[e]	20	0.5	0.5	21	68
10[f]	20	0.5	0.5	51	3
11	0	0.5	0.5	<1	0

[a] Substrate **1** (2 mmol) was allowed to react with O_2 (1 atm) in the presence of catalyst in acetic acid (5 ml) at 100 °C for 14 h.
[b] Conversion and other side-products are shown in text.
[c] Acetic acid (2 mL) was used.
[d] The reaction was carried out at 90 °C.
[e] Propionic acid was used as a solvent.
[f] Benzonitrile was used as a solvent.



Scheme 1.

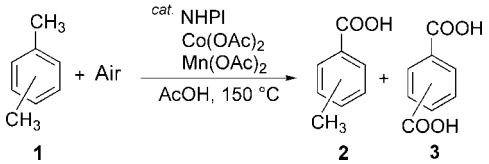
Since oxidation by use of air instead of O_2 is very important in practical industrial processes, **1** was oxidized with air using the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system (Scheme 2, Table 2). The oxidation of **1** with 20 atm of air in the presence of NHPI (20 mol %), $Co(OAc)_2$ (0.5 mol %) and $Mn(OAc)_2$ (0.5 mol %) in acetic acid at 150 °C for 3 h gave **3** (65%) together with **2** (19%) and 4-CBA (4%) (run 1). When the reaction was carried out under pressure of air (30 atm), the yield of **3** reached 84%. In this oxidation, the yield of 4-CBA was less than 1% (run 2). When the amount of NHPI was decreased to 15 mol %, **3** was formed in almost the same yield as that by 20 mol % (run 3). Both *o*- and *m*-xylenes were also successfully converted into the corresponding dicarboxylic acids under these reaction conditions, affording isophthalic

Table 2. Oxidation of xylenes catalyzed by NHPI[a]

Run	Substrate	Air (atm)	NHPI (mol %)	Yield (%)	
				2	**3**
1	*p*-Xylene (**1**)	20	20	19	65
2	**1**	30	20	1	84
3	**1**	30	15	4	84
4	**1**	30	10	14	71
5	*m*-Xylene	30	15	7	87
6[b]	*o*-Xylene	30	15	6	73

[a] The reaction was carried out in 50 mL stainless autoclave. Xylene (2 mmol) was allowed to react in the presence of NHPI, $Co(OAc)_2$ (0.5 mol %), and $Mn(OAc)_2$ (0.5 mol %) under pressure of air in acetic acid (3 mL) at 150 °C for 3 h.
[b] 2-Carboxybenzyl alcohol (8%) and 2-carboxybenzaldehyde (3%) were also produced (see Experimental Section).

acid and phthalic acid in 87% and 73% yields, respectively (runs 5 and 6).



Scheme 2.

As reported previously, toluene was smoothly oxidized under normal temperature and pressure of dioxygen (25 °C, 1 atm of O_2) by the combined catalytic system of NHPI with $Co(OAc)_2$. However, the oxidation of **1** by the NHPI/$Co(OAc)_2$ system produced **3** in a lower yield than that obtained by the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system. Hence, the effect of the Mn salt on the present oxidation was examined (Figure 1 and Figure 2). As shown in Figure 1, the yield of **3** by the oxidation of **1** using the NHPI/$Co(OAc)_2$ catalyst was 67%, but the addition of 0.1 mol % of $Mn(OAc)_2$ to the NHPI/$Co(OAc)_2$ system resulted in **3** in 75% yield. The yield of **3** reached to 82% by the addition of 0.5 mol % of $Mn(OAc)_2$, but no acceleration was observed upon further addition of $Mn(OAc)_2$.

Time-dependence curves for the aerobic oxidation of **1** by the NHPI/$Co(OAc)_2$ system were compared

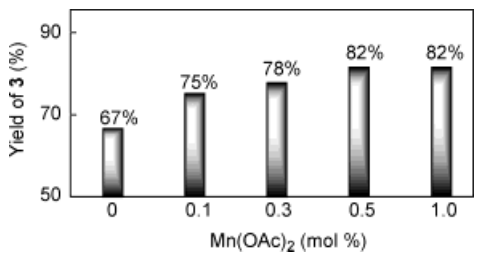


Figure 1. Addition effect of $Mn(OAc)_2$ to NHPI/$Co(OAc)_2$ system. Conditions: Substrate **1** (2 mmol) was allowed to react under O_2 (1 atm) in the presence of NHPI (20 mol %) and $Co(OAc)_2$ (0.5 mol %) in acetic acid (5 mL) at 100 °C for 14 h.

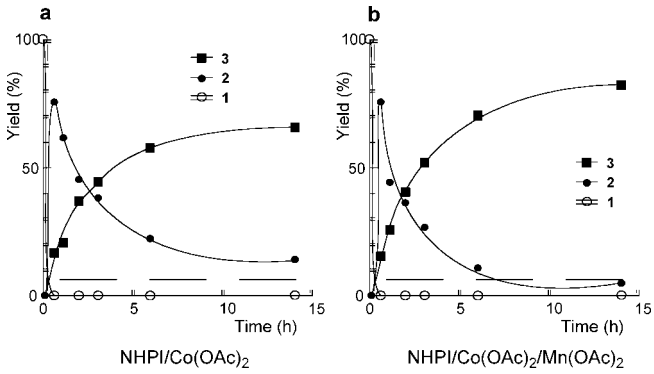
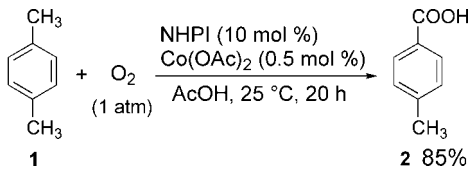


Figure 2. Time-dependence curves for the aerobic oxidation of **1** catalyzed by NHPI. (**a**) **1** (2 mmol) was allowed to react with O_2 (1 atm) in the presence of NHPI (20 mol %) and $Co(OAc)_2$ (0.5 mol %) in acetic acid (5 ml) at 100 °C. (**b**) **1** (2 mmol) was allowed to react with O_2 (1 atm) in the presence of NHPI (20 mol %), $Co(OAc)_2$ (0.5 mol %), and Mn (0.5 mol %) in acetic acid (5 mL) at 100 °C.

with that from the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system (Figure 2). With both catalytic systems, **1** was found to be consumed within 0.5 h, and **2** was formed in the range of 73% to 75% yields. Subsequently, **2** was gradually converted into **3** in 82% yield by the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ and in 67% yield by the NHPI/$Co(OAc)_2$ systems, respectively. In the conventional autoxidation of *p*-xylene, a similar enhancement by the Mn salt has been observed.[1–3] The synergistic effect of Co(II) and Mn(II) is reported to lead to a reduction of the induction period and to an enhancement of the rate in the chain-propagation step.[7] Unfortunately, in the oxidation by the NHPI/Co(II)/Mn(II) system, the effect of Mn(II) on the rate enhancement cannot be described at the present time.

Production of TPA via Two Steps from *p*-Xylene

As mentioned in the introduction, Dynamit-Nobel (Witten) manufactures dimethyl terephthalate (DMT) from *p*-xylene **1** according to the following steps: *p*-xylene → *p*-toluic acid → methyl *p*-toluate → monomethyl terephthalate → DMT. In a previous paper, we showed that *p*-xylene **1** was oxidized by the NHPI/$Co(OAc)_2$ system under a normal pressure of O_2 even at room temperature to form *p*-toluic acid **2** in 85% yield (Scheme 3). The conversion of **1** to **2** at room temperature is thought to be very interesting. Therefore, we next tried the NHPI-catalyzed oxidation of **2** and methyl *p*-toluate (**4**) derived from the oxidation of **1** at room temperature.



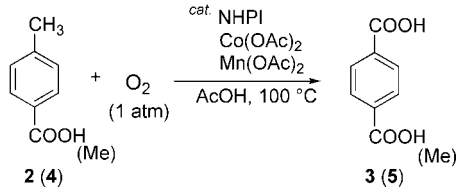
Scheme 3.

Table 3. Oxidation of *p*-toluic acid (**2**) or methyl *p*-toluate (**4**) catalyzed by NHPI[a]

Run	Catalyst (mol %)			Conversion (%)	Yield (%)[b]
	NHPI	$Co(OAc)_2$	$Mn(OAc)_2$		
1[c]	10	0.5	0.5	99 (99)	94 (92)
2	5	0.5	0.5	94 (95)	86 (88)
3	3	0.5	0.5	74	71
4	10	0.5	–	94	86
5	10	0.5	0.1	99	93
6[d]	5	0.5	0.5	99 (99)	95 (93)

[a] Compound **2** (or **4**) was allowed to react with O_2 (1 atm) in the presence of catalyst in acetic acid (5 mL) at 100 °C for 14 h.
[b] The number in the parenthesis shows the conversion and yield in the oxidation of **4**.
[c] The amount of 4-CBA was less than 1%.
[d] Compound **2** (or **4**) was allowed to react under pressure of air (30 atm) in the presence of catalyst in acetic acid (3 mL) at 150 °C for 3 h. Side products other than **3** (**5**) were mainly 4-CBA, 4-carboxybenzyl alcohol, and 4-acetoxymethylbenzoic acid.

p-Toluic acid (**2**) or methyl *p*-toluate (**4**) was allowed to react under dioxygen atmosphere (1 atm) in the presence of NHPI (10 mol %), $Co(OAc)_2$ (0.5 mol %), and $Mn(OAc)_2$ (0.5 mol %) in acetic acid at 100 °C for 14 h to give terephthalic acid (**3**) or monomethyl terephthalate (**5**) in 94 or 92% yield, respectively, along with a small amount (< 1%) of 4-CBA (Scheme 4 and Table 3, run 1). It is worthy of note that the oxidation successfully took place even by the use of 5 mol % of NHPI forming **3** in 86% yield (run 2). A remarkable enhancement of the oxidation was observed by the addition of an Mn salt to the NHPI/$Co(OAc)_2$ system (runs 4 and 5). When the reaction was carried out under pressure of air (30 atm) at 150 °C, the oxidation of **2** was completed within 3 h to afford **3** in excellent yield (run 6). Compound **4** was also oxidized with ease under these reaction conditions. Treatment of **4** under pressure of air (30 atm) by the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system in acetic acid at 150 °C for 3 h gave **5** in 93% yield (run 6).



Scheme 4.

Oxidation of *p*-Xylene Catalyzed by *N*-Acetoxyphthalimide

As shown in Table 1, ca. 20 mol % of NHPI must be used to convert *p*-xylene **1** into terephthalic acid **3** in satisfactory yield (over 80%). This is believed to be due to the gradual decomposition of the NHPI to inert phthalimide and phthalic anhydride during the oxidation. Our efforts were directed to the reduction of the amount of the catalyst employed in this oxidation, and *N*-acetoxyphthalimide (NAPI) was found to be an efficient catalyst. Table 4 shows the results for the oxidation of **1** with molecular oxygen by the use of NAPI instead of NHPI. The oxidation of **1** in the presence of catalytic amounts of NAPI (20 mol %), $Co(OAc)_2$ (0.5 mol %), and $Mn(OAc)_2$ (0.5 mol %) by dioxygen (1 atm) in acetic acid at 100 °C for 14 h afforded **3** in excellent yield (92%) together with **2** (1%) and 4-CBA (1%) (run 1). Almost the same results were obtained when the oxidation was carried out in the absence of $Mn(OAc)_2$ (run 2). Interestingly, **1** was oxidized to **3** in high yield even by the use of 10 mol % of NAPI (run 4). The oxidation in the presence of NAPI (5 mol %), $Co(OAc)_2$ (0.5 mol %), and Mn (0.5 mol %) afforded **3** (80%), **2** (8%), and 4-CBA (5%) (run 6). In a 10 mmol scale experiment under the same reaction conditions as the run 4, **3** was obtained in 80% yield (run 7).

Table 4. Oxidation of *p*-xylene (**1**) catalyzed by NAPI[a]

Run	Catalyst (mol %)			Yield (%)	
	NAPI	$Co(OAc)_2$	$Mn(OAc)_2$	**2**	**3**
1	20	0.5	0.5	1	92
2	20	0.5	–	1	91
3	10	0.5	–	48	38
4[b]	10	0.5	–	1	89
5[b]	5	0.5	–	53	24
6[b]	5	0.5	0.5	8	80
7[c]	10	0.5	–	6	80
8[d]	5	0.5	–	4	88

[a] Compound **1** (2 mmol) was allowed to react with O_2 (1 atm) in the presence of catalyst in acetic acid (5 mL) at 100 °C for 14 h.
[b] Acetic acid (2 mL) was used.
[c] Compound **1** (10 mmol) and acetic acid (10 mL) were used.
[d] Compound **1** (2 mmol) was allowed to react under pressure of air (30 atm) in the presence of catalyst in acetic acid (2 mL) at 150 °C for 3 h.

Figure 3 shows the time-dependence curves for the aerobic oxidation of **1** catalyzed by NAPI combined with $Co(OAc)_2$. In contrast to the oxidation of **1** by NHPI where **1** was completely consumed within 1 h (Figure 2), the analogous oxidation of **1** by NAPI proceeded much more slowly. This observation suggests that oxidation of **1** at the early stage of the reaction triggered the decomposition of the NHPI to phthalimide and phthalic anhydride. Although it is rather difficult to explain the effect of the NAPI in this oxidation, it was found that the NAPI gradually generates NHPI by hydrolysis with H_2O formed during the oxidation as well as involving acetic acid. Therefore, the NAPI may be suppressing the decomposition to phthalimide or phthalic anhydride by gradually supplying NHPI during the oxidation.

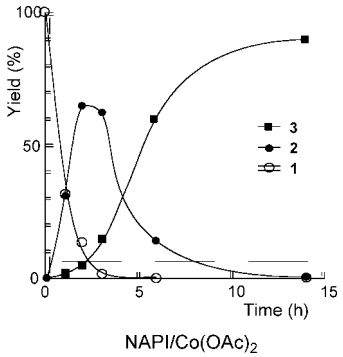


Figure 3. Time-dependence curves for the aerobic oxidation of **1** catalyzed by NAPI. Conditions: **1** (2 mmol) was allowed to react with O_2 (1 atm) in the presence of NAPI (10 mol %) and $Co(OAc)_2$ (0.5 mol %) in acetic acid (2 mL) at 100 °C.

In conclusion, a new strategy for the aerobic oxidation of *p*-xylene to terephthalic acid has been examined by the use of a combined catalyst system of NHPI (or NAPI) with $Co(OAc)_2$ and $Mn(OAc)_2$. The present method provides the direct oxidation of **1** to **3** and two-step production to **3** through **2** from **1**. These oxidations could be carried out under relatively mild conditions without any halogen ion.

Experimental Section

General

All starting materials and catalysts were purchased from commercial sources and used without further treatment. The yield of **3** was isolated yield from the reaction mixtures. The yields of **2** and **5** were estimated from the peak areas based on the internal standard technique by using HPLC. GC analysis was performed with a flame ionization detector using a 0.2 mm×25 m capillary column (OV-1). ^1H and ^{13}C NMR spectra were measured at 270 MHz and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. GC-MS were obtained at an ionization energy of 70 eV. All products were identified by comparison of the isolated products with authentic samples.

General Procedure for Oxidation of 1 or 2 under Dioxygen Atmosphere

An acetic acid solution (5 mL) of substrate (2 mmol), NHPI (20 mol %, 0.4 mmol), $Co(OAc)_2$ (0.5 mol %, 0.01 mmol), and $Mn(OAc)_2$ (0.5 mol %, 0.01 mmol) was placed in a three-necked flask equipped with a balloon filled with O_2. **Caution**: *A balloon filled with oxygen can be hazardous, even with a small-scale reaction*. The mixture was stirred at 100 °C for 14 h. After the reaction, a white precipitate including terephthalic acid (**3**) was formed. The solid was filtered off under vacuum, and washed with acetic acid several times to give almost pure terephthalic acid. For analysis by HPLC, the reaction mixture was added to ca. 150 mL of aqueous $NaHCO_3$ and then a buffer solution (20 mol/L of K_2HPO_4 and KH_2PO_4 in water) was added.

General Procedure for Oxidation of 1 or 2 under Pressure of Air (30 atm)

The reaction was carried out in 50-mL stainless steel autoclave. An acetic acid solution (3 mL) of substrate (2 mmol), NHPI (5 mol %, 0.1 mmol), $Co(OAc)_2$ (0.5 mol %, 0.01 mmol), and $Mn(OAc)_2$ (0.5 mol %, 0.01 mmol) was placed in an autoclave. The autoclave was pressurized to 30 atm with air. The mixture was stirred at 150 °C for 3 h. The work-up was performed as described above.

Procedure for the Oxidation of *o*-Xylene under Pressure of Air (30 atm)

After the oxidation of *o*-xylene as described above, the solvent was evaporated under reduced pressure. Then the reaction mixture was treated with NaOH (15 mmol) in H_2O (30 mL) at 90 °C overnight in order to hydrolyse phthalic anhydride, which was formed as a by-product, giving phthalic acid isolated in 73% yield.

Acknowledgements

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