# Synthesis of Terephthalic Acid by p-Cymene Oxidation using Oxygen: Toward a More Sustainable Production of Bio-Polyethylene Terephthalate

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The synthesis of terephthalic acid from biomass remains an unsolved challenge. In this study, we conducted the selective oxidation of *p*-cymene (synthesized from biodegradable terpenes, limonene, or eucalyptol) into terephthalic acid over a Mn–Fe mixed-oxide heterogeneous catalyst. The impact of various

Introduction

Today, the global consumption of terephthalic acid (TA), one of the monomers for the production of polyethylene terephthalate (PET), is over 60 million tons. Nearly all of this is used for the manufacture of PET,<sup>[1]</sup> which is one of the most ubiquitous industrial polymers used in the production of clear bottles for beverages, molded containers, and other packaging materials as well as in polyester films and fibers. TA is produced on an industrial scale by the oxidation of *p*-xylene through the Amoco-MC process.<sup>[2,3]</sup>

To develop more-sustainable products, several companies are searching for biobased polymers to replace those currently produced from fossil resources. The global biobased PET market is expected to grow by up to 68% from 2015 to 2019, several companies seeking to manufacture biobased TA. One possible option is the replacement of petro-based TA with biobased 2,5-furandicarboxylic acid, which can be obtained from carbohydrates; in this case, polyethylene furanoate (PEF) would replace PET.<sup>[4]</sup> However, there are still several issues to be solved in the synthesis of new biopolymers. Indeed, the most convenient alternative would be the development of a process for the production of biobased TA, which would make it possible to keep the current market for bio-PET.

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process parameters (oxidant, temperature, reaction time, catalyst amount, oxygen pressure) on the selectivity to terephthalic acid was evaluated, and some mechanistic aspects were elucidated. An unprecedented synthesis of biobased terephthalic acid (51% yield) in the presence of  $O_2$  is reported.

The only study of the synthesis of p-toluic acid from pcymene was reported 80 years ago, but there are no reports concerning the one-step oxidation to TA.<sup>[5]</sup> p-Cymene is classified as an alkylbenzene related to a monoterpene. One of the most important features of *p*-cymene is that it can be synthesized with low-cost technology from biodegradable terpenes, limonene, or eucalyptol.<sup>[6-8]</sup> Limonene comes from agricultural waste such as orange peel, and eucalyptol is the main chemical component in eucalyptus oil, which is extracted from the leaves of the Eucalyptus tree; therefore, p-cymene can be considered to be a reliable renewable resource.<sup>[6,9]</sup> Although there are several directions to valorize both limonene and eucalyptol, the global market size (e.g., estimated at over 45 kt for D-limonene in 2015 and anticipated to exceed 65 kt by 2023) may allow the replacement of the 60 million tons of TA produced annually from *p*-xylene by a small fraction of biosourced TA (and PET). This is in view of the foreseen EU restrictions that might be issued regarding the production of renewable-based polymers.

Moreover, the selective oxidation of *p*-cymene is a challenging topic of research today. Indeed, the reaction products have a multitude of applications: *p*-methylacetophenone is a precursor for the manufacture of perfumes; *p*-isopropylbenzyl alcohol is used for flavoring; cuminaldehyde is used as a flavoring agent in the food sector; *p*-isopropylbenzoic acid is used for flavors and fragrances, as a corrosion inhibitor, and a medicinal intermediate; *p*-tolualdehyde, *p*,*α*-dimethylstyrene, *p*-toluic acid, and *p*-cymenol are intermediates in various sectors; and primary and tertiary cymene hydroperoxides are rubber polymerization initiators.<sup>[7,10]</sup>

Although the first studies dealing with the selective oxidation of *p*-cymene began more than 80 years ago<sup>[5]</sup> and several studies have been reported since then, no significant research progress has been achieved using heterogeneous catalysts, although many homogeneous methods have been reported.<sup>[11,12]</sup> In a SABIC study, biobased TA was synthesized by first convert-



ing terpene to *p*-cymene and then oxidizing the latter by a two-step process; a mineral acid was used in the first step, and a transition-metal oxidant, such as a permanganate compound, was used in the second step.<sup>[8]</sup> Thus, new pathways for the production of biobased TA that avoid the use of toxic reagents should be found. In this regard, the greatest consideration should be given to the heterogeneous catalytic oxidation of *p*-cymene with O<sub>2</sub>, as the use of heterogeneous catalysts enables the shift of existing technologies to more-sustainable processes.<sup>[13]</sup>

An overview of existing studies on the heterogeneous oxidation of p-cymene reveals the existence of different catalyst formulations for such reactions. In 1932, Stubbs presented the aerobic liquid-phase oxidation of p-cymene in the presence of a manganese dioxide catalyst to form 33% p-methylacetophenone and 40% p-toluic acid at 160°C.<sup>[5]</sup> Makgwane et al. studied the oxidation of p-cymene in the liquid phase using the well-known V/P/O catalyst for gas-phase oxidation and obtained tert-cumyl hydroperoxide with 80% selectivity, which could be further used to produce *p*-methylacetophenone or TA.<sup>[14]</sup> Vetrivel and Pandurangan obtained 4-methylacetophenone, 4-isopropylbenzaldehyde, 1,2-epoxyisopropylbenzaldehyde, and 4-methylstyrene as major products over Mn/SiO<sub>2</sub>, Mn-MCM-41, and Mn-Al-MCM-41 catalysts.<sup>[15]</sup> p-Methylacetophenone (48%) was the major product obtained in the liquidphase oxidation of p-cymene (35% conversion) in the presence of BW<sub>11</sub>Fe with H<sub>2</sub>O<sub>2</sub> as the oxidizing agent at 80 °C.<sup>[16]</sup> Recently, Ru deposited on carbon nanofibers (CNFs) was also used in the aerobic oxidation of *p*-cymene, and *tert*-cymene hydroperoxide and primary cymene hydroperoxide were obtained as the major products.<sup>[17]</sup>

Very few results for the oxidation of *p*-cymene with oxygen have been reported, and random results have been obtained with no clues about the reaction mechanism. Therefore, in this study, we propose to clarify some mechanistic aspects for the selective oxidation of *p*-cymene with  $O_2$  in the presence of

a Mn–Fe mixed-oxide heterogeneous catalyst. This catalyst was chosen because  $Mn^{2+}$  ions are one of the main components of the industrial catalyst for the oxidation of *p*-xylene to TA and because the incorporation of Fe<sup>3+</sup> ions in manganese oxide enhances its redox properties.<sup>[17–19]</sup> The role of Mn in Co/Fe/O spinel-type oxides as an electron/O<sup>2-</sup> ion carrier in the chemical-loop reforming of ethanol was also recently investigated, and Mn affects the redox properties of the spinel.<sup>[20]</sup>

For the first time, we demonstrate the possibility to obtain biobased TA from p-cymene with  $O_2$  as the oxidant and assess the impact of various process parameters on the selectivity to TA.

### **Results and Discussion**

#### **Catalytic results**

The investigated Mn/Fe/O catalyst was prepared following a reported procedure,<sup>[19]</sup> which is described in the Experimental Section. This catalyst showed very good activity in 5-hydroxy-methylfurfural oxidation. Encouraged by these results, we extended our investigation to the oxidation of *p*-cymene. Its synthesis was achieved by an original, simple, and inexpensive coprecipitation approach (see the Supporting Information for full experimental details). The characterization of the catalyst is also presented in the Supporting Information.

The results for the oxidation of *p*-cymene over the Mn/Fe/O mixed-oxide catalyst suggested that the reaction occurs through a pathway that includes several parallel and consecutive reactions in which methyl and isopropyl groups are both oxidized to form the products presented in Scheme 1. Accordingly, two reaction pathways may be envisaged: a) oxidation of the methyl group to form cuminaldehyde (CA) and *p*-isopropyl benzoic acid (IBA); and b) oxidation of the isopropyl group to form tertiary cymene hydroperoxide (TCHP), *p*-cymenol (COL), *p*, $\alpha$ -dimethylstyrene (DMS), *p*-methylacetophenone (MAP), *p*-



Scheme 1. Products identified in the oxidation of *p*-cymene with Mn/Fe/O catalyst.

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tolualdehyde (TALD), and p-toluic acid (TOA). TA was the end product of this consecutive oxidation, and was obtained only under certain reaction conditions.

The variable selectivity to TA with temperature and O<sub>2</sub> pressure is shown in Figure 1. The increased selectivity corresponds to the narrowing of the reaction parameters, and the best selectivity (38%) was reached at 140°C and 20 bar of O2, conditions under which the *p*-cymene was converted completely. The influence of these parameters is presented in more detail in Table 1.



Figure 1. Variable selectivity to TA based on temperature and pressure with Mn/Fe/O as catalyst; reaction conditions: p-cymene (6 mmol), catalyst (50 mg), no solvent, 24 h reaction time, 18 mL autoclave volume.

Previous studies also confirmed the stability of the Mn/Fe/O catalyst under aqueous conditions (water was also formed during the reaction).<sup>[19]</sup> Therefore, the oxidation of *p*-cymene with  $H_2O_2$  was also monitored (Table 1, entry 3). The use of pure MnO<sub>2</sub> is known to cause the decomposition of peroxygenated compounds to oxygen nonselectively, whereas H<sub>2</sub>O<sub>2</sub> also poisons the activity of MnO2; thus, water must be removed from the reaction mixture.<sup>[21]</sup> However, under the investigated conditions, the Mn/Fe/O catalyst was not deactivated and the methyl group was oxidized to form IBA with a selectivity of 17% (for a conversion of 50%), whereas the oxidation of the isopropyl group was limited to MAP.

Under oxygen pressure, the *p*-cymene conversion reached 82% (Table 1, entry 4), and IBA was produced with a selectivity similar to that found with  $H_2O_2$ ; the oxidation of the isopropyl group occurred only through the intermediate TCHP, which enabled the further oxidation of COL and MAP with a selectivity of 17% to TOA and 4% to TA. Irrespective of the oxidant (oxygen or  $H_2O_2$ ), the experimental data indicated that the oxidation of the isopropyl and methyl groups occurred with a molar ratio of 4.7 to 1.

Literature concerning the simultaneous oxidation of the methyl and isopropyl groups is controversial; this suggests that the process has a strong dependence on the nature of the catalyst.<sup>[22-25]</sup> There are reports indicating that the oxidation of the isopropyl group is preferred to that of the methyl group<sup>[25,26]</sup> to form a hydroperoxide mixture containing 86% of tertiary and 14% of primary isomers.<sup>[27]</sup> Under these conditions, the oxidation rate of the tertiary C-H bond was found to be 18 times higher than that of the primary C-H bond. This behavior was associated with a hyperconjugation effect involving the C–H bonds.  $^{\scriptscriptstyle [2,28]}$  Other studies, performed in the presence

table 1. Results for the oxidation of p-cymene."													
Entry	Catalyst	Т	Pop	Time	Conv.	Selectivity [%]							
	-	[°C]	[bar]	[h]	[%]	TCHP	COL	MAP	TOA	CA	IBA	TA	others
1	none	100	35	24	0	-	-	-	-	-	-	-	-
2	none	140	20	24	0	-	-	-	-	-	-	-	-
3	Mn/Fe/O <sup>[b]</sup>	100	-	6	50	22	34	27	0	0	17	0	0
4	Mn/Fe/O	100	35	6	82	16	6	36	17	0	18	4	3
5	Mn/Fe/O	100	8	6	68	19	42	19	0	0	19	4	1
6	Mn/Fe/O	100	20	6	82	18	21	26	5	0	23	5	2
7	Mn/Fe/O	80	20	6	65	0	53	14	0	0	18	0	15
8	Mn/Fe/O	100	20	24	85	16	7	40	9	0	20	5	3
9	Mn/Fe/O	140	20	6	99	0	0	0	75	0	13	12	0
10	Mn/Fe/O	140	20	24	100	0	0	0	56	0	5	38	0
11	Mn/Fe/O	100	35	1	28	34	41	8	0	15	0	0	2
12	Mn/Fe/O	100	35	2	76	13	40	22	0	0	21	4	0
13	Mn/Fe/O	100	35	3	80	18	28	23	0	0	25	5	1
14	Mn/Fe/O	100	35	24	85	16	3	40	19	0	15	5	2
15	none	140	-	24	0	-	-	-	-	-	-	-	-
16	Mn/Fe/O	140	35	6	_[c]	-	-	-	-	-	-	-	-
17	Mn/Fe/O	160	20	6	_ <sup>[c]</sup>	-	-	-	-	-	-	-	-
18	Mn/Fe/O <sup>[d]</sup>	140	20	24	100	0	0	0	40	0	5	51	4
19	Mn/Fe/O <sup>[d]</sup>	140	20	48	100	0	0	0	40	0	5	51	4

[a] Reaction conditions: p-cymene (6 mmol), catalyst (50 mg), no solvent, 18 mL autoclave volume. [b] H<sub>2</sub>O<sub>2</sub> (12 mmol). [c] The reaction mixture exploded under these conditions (140 °C and 35 bar; 160 °C and 20 bar), probably because of the rapid formation of high amounts of TALD, which is highly inflammable; only black carbon was observed after the reaction; the results could not be quantified. For safety, we advise that the oxidation of p-cymene is not performed under these harsh reaction conditions.[d] p-Cymene (3 mmol), catalyst (25 mg), no solvent, 28 mL autoclave volume.

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of oxygen, supported the preferential oxidation of the methyl group, with the primary hydroperoxide produced being readily converted into products such as p-isopropylbenzyl alcohol, CA, and IBA. For example, in the homogeneous catalytic Co-based oxidation of *p*-cymene, the methyl group reacts approximately 19 times faster than the isopropyl group as a consequence of an electron-transfer mechanism involving a radical cation as an intermediate.<sup>[12]</sup> In terms of selectivity, the reactivity of the isopropyl group in p-cymene is represented by half the molar amount of p-acetylbenzoic acid formed, whereas the reactivity of the methyl group is represented by the sum of IBA and half the amount of *p*-acetylbenzoic acid produced. Under these conditions, the addition of chloride ions changed the reactivity and reaction mechanism, whereas the oxidation of the isopropyl group relative to the methyl group occurred in a ratio of 3.2 to 1, which typically corresponds to a free-radical oxidation of p-cymene.[25,29] On the basis of these reports, one may assume that the ratio of 4.7 obtained in this study may account for a free-radical mechanism.

The selectivity of the reaction was influenced strongly by the reaction conditions (Table 1). The increase in  $O_2$  pressure from 8 to 35 bar was conducive to a more advanced oxidation of the isopropyl group to TOA and MAP, to the detriment of the yield of COL (Table 1, entries 4–6), which is a common intermediate for TOA and MAP formation. However, this did not affect the ratio between the products with oxidized methyl and isopropyl groups. The increase did not influence the selectivity to TA either.

The increase in  $O_2$  pressure from 8 to 20 bar (Table 1, entries 5 and 6) led to an increased conversion of *p*-cymene, with a further increase in the  $O_2$  pressure to 35 bar promoting the conversion of intermediates and not the conversion of *p*-cymene (Table 1, entry 4). Overall, the reaction was clearly limited by the amount of  $O_2$  loaded, which was substoichiometric.

The influence of temperature was studied at three different values (80, 100, and 140  $^{\circ}$ C), and the respective results are depicted in Table 1, entries 6, 7, and 9. In general, the *p*-cymene conversion decreased with the decrease in reaction temperature. However, more byproducts formed at higher temperatures.

At 80 °C, the selectivity to COL (53%) was fairly high, and only 14% of MAP was obtained (Table 1, entry 7). Further increases in temperature enhanced the oxidation, leading to the formation of both TOA and TA. A sharp increase in the selectivity to TOA (from 5 to 75%) was recorded as the temperature increased from 100 to 140 °C. Under the same conditions, the selectivity to TA changed from 5 to 12% (Table 1, entries 6 and 9). A prolonged reaction time (24 h) led to a 38% selectivity in TA for a complete *p*-cymene conversion (Table 1, entry 10). This result seems particularly important as in the presence of  $O_2$  TA was produced in the absence of either a solvent (i.e., acetic acid or similar) or initiators.

At constant temperature  $(100 \,^{\circ}\text{C})$  and prolonged reaction time (Table 1, entries 6 and 8), at which the conversion of *p*-cymene reached a plateau, the changes in the distribution of products corresponded to the transformation of the intermediates included in Scheme 1. COL was oxidized to MAP and, to

a lesser extent, TOA, whereas the TCHP content was not affected very much. This may suggest that the formation of the hydroperoxide is fast under these conditions whereas the consecutive reaction pathway leading to TOA via COL and MAP is slower, requiring longer reaction times. At 140 °C (Table 1, entries 9 and 10), at complete conversion of *p*-cymene, no residual TCHP, COL, or MAP was detected; this result explains the measured TOA and TA content. A similar behavior was found for the pathway to TA via IBA. At 140 °C, the system reached a steady performance in 24 h. After that, no change in the product distribution was detected (Figure 2). This was due to



**Figure 2.** Product distribution as a function of time for the selective oxidation of *p*-cymene at 140 °C; reaction conditions: *p*-cymene (6 mmol), catalyst (50 mg), 20 bar  $O_2$ .

the fact that the amount of  $O_2$  was less than the stoichiometric requirement; indeed, the stoichiometric  $O_2/p$ -cymene molar ratio for the oxidation to TA (with the coproduction of two  $CO_2$  molecules and four  $H_2O$  molecules) is 6, but a feed molar ratio close to the stoichiometric one was achieved only for experiments performed at 35 bar  $O_2$  pressure (at such high pressure, however, temperatures higher than  $100^{\circ}C$  led to unsafe operation, see entries 16 and 17). Moreover, it has to be taken into account that the contact between oxygen and the reaction mixture worsened as the reaction proceeded as the two main products, TOA and TA, were solid under our reaction conditions.

If the reaction was performed at 140 °C in the presence of a higher amount of oxygen (initial  $O_2/p$ -cymene molar ratio = 8), the selectivity to TA increased to 51% (Table 1 entry 18). However, longer reaction times did not change the product distribution even under these conditions (Table 1, entry 19).

No conversion of *p*-cymene was detected in the absence of catalysts (Table 1, entries 1 and 2). In addition to the clear relationship between the conversion and the catalyst loading, the experiments performed in this study demonstrated an influence on the distribution of products (Figure 3). Low loadings led only to TCHP and COL because of the lower conversion achieved, whereas COL, MAP, and IBA were also produced at larger loadings. However, an optimal substrate/catalyst ratio has also been evidenced. Higher catalyst amounts had a small effect on the selectivity to products but with lower conversion; this may be attributed to a chain-termination effect that may



**Figure 3.** Influence of catalyst loading on the selective oxidation of *p*-cymene; reaction conditions: *p*-cymene, (6 mmol) 35 bar of  $O_{2^{2}}$  100 °C, reaction time 2 h.

occur in the presence of relatively large amounts of the catalyst initiator.  $^{\rm [30]}$ 

The catalytic performance of the Mn/Fe/O catalyst was compared to those of the constitutive oxides (i.e.,  $Mn_2O_3$  and  $Fe_2O_3$ ) and other metal oxides. The results are gathered in Table 2.

Table 2. Influence of the catalytic material on conversion and catalytic selectivity. $^{\left[ a\right] }$										
Entry	ry Catalyst Conv. Selectivity %									
		[%]	TCHP	COL	MAP	TOA	CA	IBA	TA	others
1	None	0	-	-	-	-	-	-	-	-
2	Mn/Fe/O	82	16	6	36	17	0	18	4	3
3	$Mn_2O_3$	73	17	33	50	0	0	0	0	0
4	Fe <sub>2</sub> O <sub>3</sub>	8	65	32	0	0	0	0	0	3
5	$CoFe_2O_4$	46	11	52	14	0	0	23	0	0
6	NiFe <sub>2</sub> O <sub>4</sub>	61	30	30	17	0	5	10	0	4
7	$5 \% V/AI_2O_3$	35	55	23	5	0	5	9	0	3
[a] Reaction conditions: p-cymene (6 mmol), catalyst (50 mg), 6 h, 100 $^\circ\text{C},$ 35 bar O_2, no solvent.										

 $Mn_2O_3$  showed a higher conversion (73%) than  $Fe_2O_3$  (8%; Table 2, entries 3 and 4) but lower than that of Mn/Fe/O (82%; Table 2, entry 2). However, the main issue is the major difference in selectivity. No TOA or TA was detected with these single metal oxides. For  $Mn_2O_3$ , MAP was the major product, whereas the only products were TCHP and COL with  $Fe_2O_3$ . For other oxides (NiFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, and 5%V/Al<sub>2</sub>O<sub>3</sub>; Table 2, entries 5–7), the oxidation stopped at MAP (with lower conversions).

The good activity of Mn/Fe/O is in agreement with our previous study,<sup>[19]</sup> in which we demonstrated that a mixture of Mn<sup>III</sup> and Mn<sup>IV</sup> coexists with a hematite phase. Also, as already reported, the surface basicity improved the catalyst oxidant behavior (Figure 4).<sup>[19,31]</sup> Moreover, charge-transfer transitions between iron d electrons and the manganese oxide conduction or valence bands were evidenced in the UV/Vis spectra by the redshift of the high energy band for Mn/Fe/O compared with that for Mn<sub>2</sub>O<sub>3</sub> (Figure S3).



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Figure 4. Comparative results of different catalysts from the characterization data; reaction conditions: *p*-cymene (6 mmol), catalyst (50 mg), 6 h, 100 °C, 35 bar O<sub>2</sub>, no solvent.

On the basis of these data, we assume that the efficient oxidation of *p*-cymene to TA may be attributed to a synergic cooperation of the three phases found in Mn/Fe/O together with an optimal basicity and electronic interactions between iron and manganese.

#### **Mechanistic studies**

The autoxidation of hydrocarbons proceeds by a radical chain mechanism that involves a large number of radical and molecular species.<sup>[22]</sup> In the past few years, several reviews have dealt with the chemistry of the autoxidation of alkylaromatics in the liquid phase by molecular oxygen.<sup>[23–25,32]</sup> The analysis of the oxidative steps involved in the oxidation of alkylaromatics with O<sub>2</sub> suggested either a direct hydrogen abstraction or a prior transfer of an electron to the oxidizing agent, followed by the transfer of a proton.

In view of these reports, the new Mn/Fe/O catalyst appears to be capable of accelerating the reaction rate through a freeradical chain mechanism. The first step in the oxidation is the initiation, which involves the activation of the C–H bond through the abstraction of a H atom. In the absence of any other initiator, this reaction may be started by the hydrocarbon itself [Reaction (1)].<sup>[24]</sup>



This is an endothermic and rather slow reaction; therefore, induction periods are often observed in the absence of initia-



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tors. The HO<sub>2</sub> radical is a weak acid corresponding to the protonated form of the superoxide radical ion, which can be formed readily on the surface of the oxide according to Reaction (2):<sup>[33]</sup>

The H abstraction may also occur for a superoxide species  $(O_2^{-})$  bound to a metal center or metal oxide [Reaction (3)]:<sup>[34]</sup>

$$M^{n+} + O_2 \to O - O - M^{(n+1)+}$$
 (3)

Then the 'OOH radical may react with *p*-cymene to give the peroxide [Reaction (4)]:



On this basis, Reactions (5) and (6) account for the chain propagation:



To confirm the hypothesis of a free-radical chain mechanism, we conducted catalytic tests in the presence of increasing amounts of hydroquinone (HQ) as a radical scavenger. The results are presented in Figure 5; the conversion of *p*-cymene dropped from 82 (measured in the absence of HQ) to 21% for an HQ/*p*-cymene molar ratio of only 0.01.

These results confirm that the activation and selective oxidation of p-cymene in the presence of the Mn/Fe/O catalyst occurs with the involvement and propagation of radical intermediates. Moreover, in the presence of HQ, no IBA was



Figure 5. The variation of *p*-cymene conversion with HQ/*p*-cymene molar ratio; reaction conditions: *p*-cymene (6 mmol), catalyst (50 mg), 35 bar  $O_2$ , 100 °C, 6 h.

formed; therefore, no oxidation occurred at the methyl group. By increasing the HQ/p-cymene molar ratio, the effect on the conversion was more pronounced, and *p*-cymene was no longer converted at a ratio of 0.1.

The time evolutions of the conversion and selectivity are presented in Table S2 and Figure 6. As expected, owing to the high activation energy required to break the C–H bond, in the

absence of any initiator, the generation of radicals needed an induction period (Table S2, entries 1 and 2), a phenomenon observed typically for all radical chain reactions. At 100 °C and 35 bar of O<sub>2</sub>, the conversion of p-cymene reached 28% only after 60 min (Table S2, entry 2). The conversion of p-cymene increased with the reaction time, and numerous products were released. After 60 min of reaction time, the main products were TCHP and COL (34 and 41% selectivity, respectively), along with some MAP (8%) and CA (15%) (Table S2, entry 2). At 90 min reaction time, along with the sudden increase in conversion, which is typical for radical chain reactions necessitating an initiation step, the main product was COL. After 120 min reaction time (Table S2, entry 4), no residual CA was found; the disappearance of CA was due to its further oxidation to IBA. Thus, the radical chain mechanism occurred mainly with an attack on the tertiary C atom and the formation of TCHP, COL, MAP, and TOA; these compounds exhibited a typically

consecutive reaction pattern, in which the decrease in selectivity to COL (formed by the decomposition of TCHP) occurred with a concomitant increase in selectivity to MAP. TOA was the product formed later along this reaction pattern, as shown by its selectivity, which became greater than zero only for reaction times of at least 6 h and then increased continuously.

For the oxidation of the primary C atom, the first product observed was CA with 15% selectivity at 60 min reaction time; however, it immediately reacted to form IBA, the selectivity of which increased until a maximum of approximately 20%.

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**Figure 6.** Influence of the reaction time on the selective oxidation of *p*-cymene; reaction conditions: *p*-cymene (6 mmol), catalyst (50 mg), 35 bar  $O_{2^{\prime}}$  100 °C.

Lastly, the formation of the desired product, TA, only occurred to a limited extent with a selectivity of 4-5% after 90 min through the consecutive oxidation of both TOA and IBA.

A similar behavior was reported for the oxidation of *p*-xylene, for which only one methyl group was oxidized to a carboxylic acid. The  $\sigma$ + Hammett constant of the *para* substituent changes from -0.31 for the methyl group to +0.42 for the carboxylic acid; this determines a reduction in the ring electron density, which results in a slowdown of the oxidation of the second methyl group (five times slower).<sup>[2]</sup>

The individual oxidations of the intermediates, such as TCHP, DMS, CA, TALD, and MAP, were performed to clarify the origin of the products identified in the *p*-cymene oxidation. The results are depicted in Scheme 3 and represented schematically in Figure 7.

Hydroperoxides are the first oxidation products in such reactions,<sup>[35]</sup> and tertiary peroxy radicals terminate reaction chains less readily than primary peroxy radicals, as they lack a hydrogen atom at the  $\alpha$ -C atom.<sup>[28,36]</sup> In our case, TCHP was the only hydroperoxide detectable (Figure 7a). However, the presence of CA and IBA provided indirect evidence of the formation of the primary hydroperoxide (PCHP; Table S2, entries 3 and 4; Figure 7b).

It was also reported<sup>[36]</sup> that the tertiary cymene alkoxy radical may undergo different transformations: (i) decomposition to  $COL^{[27]}$  or dimerization,<sup>[28]</sup> (ii) disproportionation to generate DMS, TCHP, and O<sub>2</sub> (Scheme 2a); (iii) decomposition of TCHP into the corresponding aldehyde (with the loss of one C atom, which undergoes oxidation to  $CO/CO_2$ ) and recombination of the aldehyde with another TCHP molecule

to form MAP and TOA<sup>[37]</sup> (Scheme 2b) with the loss of two C atoms and the formation of  $CO/CO_2$ ; or (iv) abstraction of a hydrogen atom from the substrate to form TCHP. In our experiments, TCHP was oxidized to afford COL, DMS, MAP, TALD, and TOA (Scheme 3 a).

The disproportionation of TCHP was also evidenced at short reaction times and low conversions, as only MAP, DMS, and TALD were formed (Scheme 3 b). The oxidation of COL led only to DMS and TALD in a ratio of 1:3 (Scheme 3 b; Figure 7 c). If the reaction started from *p*-cymene, DMS and TALD were not identified, most probably because of the complete conversion of DMS into MAP (Scheme 3 c) and TALD into TOA (Scheme 3 e; Figure 7 c). The formation of IBA is possible most probably through CA, as is evidenced in Scheme 3 d. The formation of MAP is also possible through the decomposition of TCHP and the oxidation of DMS. The high MAP content in the reaction products may also be explained by a slow reactivity in a consecutive oxidation at 100°C (Scheme 3 f). TOA formation occurs through the oxidation of TALD, as underscored by the individual oxidation of this compound.

The individual oxidation of MAP led to TOA with 100% selectivity, only if the temperature was increased to  $140^{\circ}C$  (Scheme 3 f); therefore, the consecutive transformation of MAP into TOA is a slow step at  $100^{\circ}C$  and requires a higher temperature to occur.



**Scheme 2.** a) Disproportionation and b) decomposition of TCHP (intermediate of *p*-cymene oxidation).

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Figure 7. Oxidation of different substrates using Mn/Fe/O catalyst: a) hydroperoxide formation; b) oxidation at the methyl group; c) oxidation at the isopropyl group; reaction conditions: substrate (6 mmol), catalyst (50 mg), 35 bar  $O_2$ , 100 °C, 6 h. The dotted arrows represent the unperformed reactions.

It is worth mentioning that no 4-carboxybenzaldehyde was formed under our reaction conditions. This is an interesting result for the industrial production of pure TA, as 4-carboxybenzaldehyde is a chain-terminator during PET manufacture.<sup>[28]</sup> On the basis of all of the above findings, we show the reaction pathway for *p*-cymene oxidation in the presence of Mn/Fe/O heterogeneous catalyst in Scheme 4.

### Conclusions

The results of the experiments performed in the selective oxidation of *p*-cymene with  $O_2$  have shown that a Mn/Fe mixedoxide catalyst can produce relatively high yields of terephthalic acid with an unprecedented value of 51%. The reaction network is very complex, and two reaction pathways lead to terephthalic acid, one via *p*-toluic acid and a parallel one via *p*isopropylbenzoic acid. The relative contributions of the two routes were close to 5:1, which also suggested the predominance of radical chain reactions. However, the presence of the Mn/Fe/O catalyst was crucial, and its role is to accelerate the slowest steps in the reaction sequence leading to the monoand dicarboxylic acids. The reference catalyst  $Mn_2O_3$  provided a slightly lower conversion rate and selectivity to intermediate oxidation products but no formation of terephthalic acid. The other oxides investigated could not accelerate the slowest steps.

### **Experimental Section**

**Catalyst preparation**: The Mn/Fe/O catalyst was prepared by a coprecipitation method. First, aqueous solutions of manganese nitrate (Sigma–Aldrich) and iron nitrate (Sigma–Aldrich,  $\geq$  98%) were mixed. To the resulting solution at room temperature, an appropriate volume of NaOH and Na<sub>2</sub>CO<sub>3</sub> solution (1.5 M) was added to the well-stirred flask to maintain the pH at 9–10. The precipitate was aged overnight at 75 °C under stirring. The precipitate was collected by filtration, washed thoroughly until pH 7, and dried overnight at 100 °C in an oven. The mixed oxide was then calcined at 460 °C for 18 h in air. For comparison, pure manganese and iron oxides were also prepared by the same procedure. The atomic ratio between the two elements was Mn/Fe=3:1.

**Catalyst characterization**: The samples were investigated by powder X-ray diffraction and textural analysis. The XRD patterns



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Scheme 3. Oxidation of different substrates using Mn/Fe/O as catalyst; reaction conditions: substrate (6 mmol), catalyst (50 mg), 35 bar O<sub>2</sub>, 100 °C, 6 h and 20 bar  $O_2$  and  $T = 140 \,^{\circ}C$  for (f). c refers to conversion.

were recorded with a Shimadzu 7000 powder diffractometer with CuK<sub>a</sub> radiation ( $\lambda = 1.54184$  Å). The patterns were collected in the  $2\theta$  range from 5 to  $80^{\circ}$  in steps of  $0.02^{\circ}$ . The textural measurements used the  $N_2$  adsorption-desorption isotherms collected at -196 °C using a Micromeritics ASAP 2010 sorption analyzer. Before the analysis, the catalysts were outgassed at 200  $^\circ\text{C}$  in vacuum. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation.

p-Cymene oxidation procedure: The selective oxidation of pcymene ( $M = 134.22 \text{ g mol}^{-1}$ ;  $\rho = 0.8575 \text{ g cm}^{-3}$ ) was performed under several conditions of temperature, time, and pressure and with different oxidizing agents (aqueous  $\mathsf{H}_2\mathsf{O}_2$  and  $\mathsf{O}_2$ ). In the oxidation with  $H_2O_{2'}$  the procedure was as follows: *p*-cymene (6 mmol) and the catalyst (50 mg) were loaded in a round-bottom flask (5 mL) equipped with a condenser, and the mixture was heated at 100 °C under continuous magnetic stirring. Hydrogen

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**Scheme 4.** Selective oxidation pathways of *p*-Cymene with Mn/Fe/O as catalyst.

peroxide (30%) was added dropwise (0.025 mLmin<sup>-1</sup>) using a liquid pump. After 6 h, the reaction was stopped, and the mixture was cooled to room temperature. The catalyst was separated from the reaction medium, and the remaining aliquot was analyzed by  $^1\!\mathrm{H}$  and  $^{13}\!\mathrm{C}$  NMR spectroscopy, GC, and GC–MS. In the oxidation with oxygen, p-cymene (6 mmol) and the catalyst (50 mg) were loaded in a stainless-steel autoclave (18 mL). The reactor was filled with different amounts of O<sub>2</sub> at room temperature only once at the beginning of the reaction, that is, 5.6 mmol of  $O_2$  (8 bar), 13.9 mmol of  $O_2$  (20 bar), and 24.3 mmol of  $O_2$  (35 bar). Then the reactor was heated at different temperatures and times under continuous magnetic stirring. An increase of the pressure with heating was observed for all experiments. After the designated time had elapsed, the reaction was stopped, and the reactor was cooled to room temperature; a lower pressure was recorded than the starting one owing to the consumption of oxygen. The catalyst was separated from the reaction medium, and the remaining aliquot was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, GC, and GC-MS. A carbon mass balance of 80-90% was obtained depending on the reaction parameters; the difference corresponds to the carbon lost to produce CO and CO<sub>2</sub>. The analysis of the gas from the headspace was not performed. The conversion and selectivity were calculated using Equations (7) and (8).

*p*-cymene conversion (%) = 
$$(\mu_{p\text{-cymene}_{transformed}}/\mu_{p\text{-cymene}_{in}}) \times 100$$
 (7)

product selectivity (%) = 
$$(\mu_{\text{product}}/\mu_{p\text{-cymene}_{\text{transformed}}}) \times 100$$
 (8)

where  $\mu$  is number of moles. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Fourier 300 MHz spectrometer. The reactants and products were also analyzed by means of GC using a Shimadzu 2010 instrument fitted with a DB-5 capillary column (50 m, 0.2 mm) connected to a flame ionization detector (FID). The compounds were also identified by means of GC–MS using a Thermo Scientific TRACE<sup>TM</sup> Ultra Gas Chromatograph fitted with a TraceGOLD TG-

5SilMS column. The data were acquired and processed using the Thermo Scientific Xcalibur data handling software.

For the metal leaching test, the catalyst was separated by filtration, and the obtained filtrate was allowed to react further for 1 h and analyzed again. No substantial modification of the conversion was observed. Blank reactions were performed and confirmed that no oxidation products formed if the catalyst or the oxidant was not present.

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**Keywords:** carboxylic acids · heterogeneous catalysis · iron · manganese · oxidation

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# **FULL PAPERS**

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Synthesis of Terephthalic Acid by p-Cymene Oxidation using Oxygen: Toward a More Sustainable Production of Bio-Polyethylene Terephthalate



**Terrific terephthalic acid:** A Mn–Fe mixed-oxide heterogeneous catalyst is used for the selective oxidation of *p*-cymene (synthesized from biodegrad-able terpenes, limonene, or eucalyptol) into terephthalic acid in a high yield of 51% with  $O_2$  as the oxidant. The impacts of various process parameters on the selectivity to terephthalic acid are evaluated, and some mechanistic aspects are elucidated.

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