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A Study about the Use of Co or Mn-Based Nanocatalysts for Styrene Epoxidation Reaction †

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Abstract: A new catalytic system consisting of Mn or Co nanoparticles supported on different materials (celite, zeolite, activated carbon, CeO_2, ZnO, MgO, Nb_2O_5) have been studied for styrene epoxidation. The catalysts were easily prepared from commercially available starting materials. Reaction conditions were optimized by testing different solvents, reaction temperatures, oxidizing agents, and optimal catalyst loading. CoNPs/MgO and TBHP as a co-oxidant, in refluxing ACN, allowed total conversion to the epoxide with excellent yield and high selectivity.

Keywords: styrene epoxidation; Mn and Co nanocatalysts; TBHP

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1. Introduction

Epoxides are very useful synthetic intermediates as they can be easily converted into a wide variety of products through different chemical transformations on the reactive oxirane ring [1]. Despite many methodologies for the synthesis of epoxides have been reported [2], efficient and selective epoxidation of olefins remains a challenge. Currently, research is focused on easy-to-use and environmentally friendly oxidants such as O_2, TBHP, air, or H_2O_2, together with a transition metal catalyst that helps to improve the reactivity and selectivity of the oxygen transfer process [3]. In this work, Mn- or Co-based nanocatalysts have been studied for styrene epoxidation. These earth-abundant and low-cost metals are known to be part of biologically relevant complexes, such as porphyrins, with a pivotal role in oxidation reactions [1,4]. Co or Mn nanoparticles (NPs) were synthesized by fast reduction of the corresponding metal chlorides, with an excess of Li sand and a catalytic amount of an arene as an electron carrier [5]. The metal NPs thus obtained were immobilized on different materials: celite, zeolite, activated carbon, CeO_2, ZnO, MgO, and Nb_2O_5. Reaction conditions were optimized by testing different solvents (CH_2Cl_2, DMF, and ACN), reaction temperatures, oxidizing agents (O_2, H_2O_2, and TBHP), and optimal catalyst loading. The progress of the reaction was controlled by GC-MS. The use of CoNPs/MgO as the catalyst and TBHP as a co-oxidant, in refluxing ACN, allowed total conversion with high selectivity to the corresponding styrene oxide, after 24 h of reaction time.

2. Methods

2.1. General Methods

Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents were treated before use by standard methods. All starting materials were of the best available grade (Aldrich, Fluka, Merck) and were used without further purification. Commercially available cobalt(II) chloride and manganese(II) chloride were ovendried and then dried by heating with a heat gun under vacuum before use. Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) and visualized under UV light and/or using 5% phosphomolybdic acid in ethanol and by CG-MS.

2.2. Synthesis of Catalysts

A mixture of lithium powder (3.0 mmol) and DTBB (0.1 mmol) in THF was stirred at room temperature under nitrogen atmosphere. When the reaction mixture turned dark green, indicating the formation of the corresponding lithium arenide, anhydrous cobalt or manganese chloride was added (1 mmol). The resulting suspension was stirred until it turned black, indicating the formation of the metal NPs. After that, it was diluted with THF and support was added. The resulting suspension was stirred for 1 h, and then bidistilled water was added for eliminating the excess of lithium. The resulting solid was filtered under vacuum by means of a Buchner funnel and washed successively with water and acetone. Finally, the solid was dried under vacuum (5 Torr).

2.3. Styrene Epoxidation

Method A [6]: $H_2O_2/NaHCO_3$

In a Schlenk flask, the MnNPs/celite catalyst and 0.3 mmol of styrene in DMF, were shaken vigorously for 10 min at 0 °C. Then, 1 mL of $NaHCO_3$ solution and 130 μL of H_2O_2 were shaken in a flask for 10 min at 0 °C. This solution was added drop by drop into the Schlenk. The reaction mixture was stirred at working temperature. The catalyst was separated from the reaction mixture by filtration.

Method B [7]: O_2

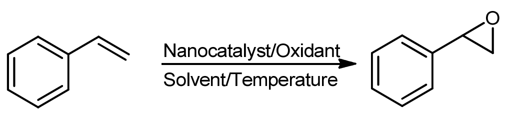
In a Schlenk flask, the MnNPs/celite catalyst was vigorously stirred in DMF or CH_2Cl_2. The reaction flask was purged and filled with oxygen. Then, 0.3 mmol of styrene was added with a syringe. The reaction mixture was stirred at working temperature. The catalyst was separated from the reaction mixture by filtration.

Method C [8]: TBHP

In a sealed flask, Co- or Mn-based nanocatalysts and 1 mL of ACN were vigorously stirred. Then, 0.3 mmol of styrene was added. Finally, 0.3 mmol of TBHP solution was slowly added and the sealed reaction flask was immersed in an oil bath at working temperature. The catalyst was separated from the reaction mixture by filtration.

3. Results and Discussion

To study the styrene epoxidation reaction (Scheme 1), as can be seen from Table 1, we started using 75 mg of MnNPs/celite as model catalyst and different oxidants, solvents, and temperatures. A very low conversion to styrene oxide (7%) was achieved, using TBHP as the oxidant, in ACN at 60 °C and a similar conversion to benzaldehyde was observed, as an oxidation by-product (Table 1—entry 7).



Scheme 1. Styrene epoxidation reaction.

Based on this result, the reaction was tested in a sealed tube, using TBHP as oxidant, in refluxing ACN (82 °C) for 24 h, improving the conversion to the epoxide (26%), although the benzaldehyde formation also was increased (Table 2—entry 1A). As can be seen from entry 1B, 2B, and 3B, a longer reaction time did not improve the conversion to the epoxide. Other MnNP catalysts were evaluated, using ceria and zeolite as supports, although it was not possible to increase the conversion to the epoxide (entries 2 and 3).

Table 1. Optimization of reaction conditions *.

Entry	Oxidant	Solvent	Temp	Styrene	Styrene Oxide	Benzaldehyde
1	$H_2O_2/NaHCO_3$	DMF	0 °C	100%	-	-
2	$H_2O_2/NaHCO_3$	DMF	RT	100%	-	-
3	O_2	CH_2Cl_2	0 °C	100%	-	-
4	O_2	DMF	0 °C	100%	-	-
5	O_2	DMF	RT	100%	-	-
6	TBHP	ACN	RT	100%	-	-
7	TBHP	ACN	60 °C	88%	7%	5%
8	TBHP	ACN/DMF (9:1)	60 °C	100%	-	-

* Time: 24 h—MnNPs/celite 75 mg.

Table 2. Study of different MnNP nanocatalysts *.

Entry	Time	Nanocatalyst	Styrene	Styrene Oxide	Benzaldehyde
1A	24 h	MnNPs/celite 75 mg	48%	26%	26%
1B	48 h		46%	27%	28%
2A	24 h	MnNPs/ceria 75 mg	50%	22%	28%
2B	48 h		51%	21%	28%
3A	24 h	MnNPs/zeolite 75 mg	63%	3%	33%
3B	48 h		18%	6%	76%

* TBHP/reflux ACN.

Then, the effective amount of MnNPs/celite catalyst required was evaluated, and the better result was obtained with 20 mg of the catalyst, yielding 43% of the epoxide and only 18% of benzaldehyde (Table 3—entry 4).

Table 3. Effective amount of MnNPs/celite nanocatalyst *.

Entry	Amount of MnNPs/Celite	Styrene	Styrene Oxide	Benzaldehyde
1	100 mg	76%	11%	13%
2	75 mg	48%	26%	26%
3	50 mg	57%	23%	20%
4	20 mg	39%	43%	18%

* TBHP/reflux ACN/Time: 24 h.

Based on the results already reported, that we mentioned above, we decided to test the reaction with cobalt as the metal of the nanocatalyst. As can be seen from Table 4, the reaction was carried out using 20 mg of the CoNPs on different supports, with TBHP as oxidant, under reflux of ACN (82 °C), for 24 h and 48 h.

In all cases, the reaction at 24 h (entries A) gave better or very similar conversions to the epoxide than the reactions at 48 h (entries B).

The reaction with 20 mg of CoNPs/celite catalyst at 24 h (Table 4—entry 1A) gave an increased conversion to the epoxide (65%), better than the same reaction using the MnNPs/celite as the nanocatalyst (43%), and almost the same amount of the oxidation by-product (Table 3—entry 4). Similar results were obtained when we employed CoNPs/zeolite as nanocatalysts (entry 3). Among all the nanocatalysts evaluated, the best conversion to the epoxide (67%) was obtained with 20 mg of the CoNPs/MgO nanocatalyst (entry 6).

Table 4. Study of different CoNP nanocatalysts *.

Entry	Time	Nanocatalyst	Styrene	Styrene Oxide	Benzaldehyde
1A	24 h	CoNPs/celite	12%	65%	23%
1B	48 h		34%	46%	20%
2A	24 h	CoNPs/ceria	67%	17%	16%
2B	48h		57%	24%	19%
3A	24 h	CoNPs/zeolite	11%	62%	27%
3B	48 h		7%	66%	27%
4A	24 h	CoNPs/C *	73%	12%	15%
4B	48 h		75%	10%	15%
5A	24 h	CoNPs/ZnO	26%	33%	41%
5B	48 h		21%	31%	48%
6A	24h	CoNPs/MgO	4%	67%	29%
6B	48 h		3%	72%	25%

* TBHP/reflux ACN/20 mg of the nanocatalyst.

Then, the effective amount of CoNPs/MgO catalyst required was evaluated, and the best results were obtained with 10 mg of the CoNPs/MgO catalyst, with total conversion, giving 91% yield of styrene oxide and only 9% yield of benzaldehyde at 24 h, thus showing excellent activity and selectivity (Table 5—entry 2). The reaction was also tested with 5 mg of nanocatalyst, and total conversion was obtained after 48 h, but lower selectivity was observed with 76% yield of styrene oxide and 24% yield of benzaldehyde (Table 5—entry 3B).

Table 5. Effective amount of CoNPs/MgO nanocatalyst *.

Entry	Time	Nanocatalyst	Styrene	Styrene Oxide	Benzaldehyde
1A	24 h	CoNPs/MgO 20 mg	4%	67%	29%
1B	48 h		3%	71%	26%
2A	24 h	CoNPs/MgO 10 mg	-	91%	9%
2B	48 h		-	95%	5%
3A	24 h	CoNPs/MgO 5 mg	10%	59%	31%
3B	48 h		-	76%	24%

* TBHP/reflux ACN.

Taking into consideration the excellent results obtained using 10 mg of the CoNPs/MgO nanocatalyst, the same conditions were used to evaluate other cobalt and manganese-based nanocatalysts. When the reaction was carried out with 10 mg of CoNPs/celite, the conversion to the styrene oxide was improved compared to the same reaction using 20 mg of nanocatalyst (74% and 65%, respectively, Table 6—entry 1 and Table 4—entry 1). The CoNPs/zeolite nanocatalyst was also evaluated, although the performance of the epoxidation did not show any improvement compared to the same reaction employing 20 mg of nanocatalyst (56% and 62% of the epoxide, respectively, Table 6—entry 2 and Table 4—entry 3). Considering the excellent performance of the MgO as support, also, the MnNPs/MgO nanocatalyst was tested, giving 66% of styrene oxide and 31% of benzaldehyde after 48 h (Table 6—entry 3B). This result was better than that obtained using MnNPs/celite (43% yield of epoxide), but not superior to that achieved with the cobalt nanocatalyst. Bearing in mind that niobium oxide has interesting redox properties, we evaluated the reaction using 10 mg of CoNPs/Nb_2O_5 as the nanocatalyst (Table 6—entry 4). The conversion was similar to that obtained with 10 mg of CoNPs/celite, but less than the conversion achieved by the CoNPs/MgO nanocatalyst.

Table 6. Study of different Co- and MnNP catalysts *.

Entry	Time	Nanocatalyst	Styrene	Styrene Oxide	Benzaldehyde
1A	24 h	CoNPs/celite	8%	74%	18%
1B	48 h		3%	79%	18%
2A	24 h	CoNPs/zeolite	16%	56%	28%
2B	48 h		10%	63%	27%
3A	24 h	MnNPs/MgO	20%	47%	33%
3B	48 h		3%	66%	31%
4A	24 h	CoNPs/Nb_2O_5	3%	73%	24%
4B	48 h		2%	72%	26%

* TBHP/reflux ACN/10 mg of the nanocatalyst.

Considering that there is evidence in the literature about a radical mechanism for the epoxidation by metal catalysis [3,9], as can be seen from Table 7 we carried out a series of reactions to confirm this assumption. Initially, the reaction was performed using 10 mg of CoNPs/MgO and TBHP under reflux of ACN for 8 h yielding 64% of the epoxide and 24% of benzaldehyde (entry 1). In the absence of the nanocatalyst, only 33% of the epoxide was obtained (entry 2). Furthermore, the reaction was tested without TBHP, with the full recovery of the starting styrene (entry 3). Finally, the reaction was carried out in the presence of hydroquinone, a known radical scavenger, and the epoxide formation was inhibited almost completely (entry 4). All these results would confirm the presence of a radical mechanism for this epoxidation reaction.

Table 7. Mechanistic study of the epoxidation reaction.

Entry	Nanocatalyst *	Additive	Oxidant	Styrene	Styrene Oxide	Benzaldehyde
1	CoNPs/MgO 10 mg	-	TBHP	12%	64%	24%
2	-	-	TBHP	53%	33%	14%
3	CoNPs/MgO 10 mg	-	-	100%	-	-
4	CoNPs/MgO 10 mg	Hydroquinone	TBHP	78%	9%	13%

* Reflux ACN/Time: 8 h.

4. Conclusions

A simple methodology has been developed for the synthesis of metallic nanocatalysts based on Co or Mn nanoparticles (NPs), which were synthesized by fast reduction of the corresponding metal chlorides, with an excess of Li sand and a catalytic amount of an arene as an electron carrier. The metal NPs thus obtained were immobilized on different supports. Reaction conditions were optimized by testing different solvents, reaction temperatures, oxidizing agents, and optimal catalyst loading. Based on the reported study, the use of 10 mg of CoNPs/MgO, as a nanocatalyst, and TBHP, as a co-oxidant, under reflux of ACN, allowed the total conversion with high selectivity to the corresponding styrene oxide, after 24 h of the reaction time. We are studying the scope of this method for the epoxidation of alkenes with a structural variety, as well as the possibility of recovery and reuse of the nanocatalysts.

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