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Short communication

## Enhancing alkane oxidation using Co-doped SnO<sub>2</sub> nanoparticles as catalysts



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#### 1. Introduction

# The development of sustainable catalytic processes for the oxidation of abundant and inexpensive alkanes into high-added-value products remains a great challenge for both academic and industrial purposes [1–4]. An example of alkane oxidation with industrial significance concerns the catalytic cyclohexane oxidation to KA oil (mixture of cyclohexanol and cyclohexanone) important to produce adipic acid and caprolactam, intermediates in polyamides manufacture [4–6]. The current industrial aerobic cyclohexane oxidation process uses a homogeneous cobalt catalyst at ca. 150 °C, forming KA oil in very low (ca. 5%) yield to achieve an acceptable selectivity. Therefore, the development of more sustainable systems operating under milder conditions is an important goal [3,4,7–9].

#### ABSTRACT

A novel eco-friendly KA oil synthesis at room temperature (up to 25% yield) via solvent-free cyclohexane oxidation using Sn<sub>1-x</sub>Co<sub>x</sub>O<sub>2- $\delta$ </sub> (x = 0, 0.01 or 0.05) nanoparticles as catalyst (TON up to  $2 \times 10^3$ ) is here reported. These nanoparticles are the first SnO<sub>2</sub>-*based* material able to catalyze the oxidation of alkanes.

The most active nanocatalyst was the  $Sn_{0.95}Co_{0.05}O_{2-\delta}$ , allowing an easy recovery and reuse, at least for five consecutive cycles, maintaining high selectivity concomitant with 92% of its initial activity.

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Nanostructured materials have attracted a great interest in recent years in a wide variety of fields, including catalysis, due to their particular physical and chemical properties [10-15]. These properties mainly depend on shape, size and structure of the materials, which are strongly determined by their synthetic processes. On the other hand, the catalytic response of a material is strongly dependent of its fundamental electronic structure, which is closely related to its chemical composition. Therefore, doping can be an important strategy to modify the catalytic activity of a nanostructured material [16–18].

 $SnO_2$  has been used in catalysis as a metal oxide support for precious metal catalysts in M/SnO<sub>2</sub> (M = Pt, Pd, Ru or Rh) systems for the combustion at low temperatures of volatile organic compounds [19]. However, to our knowledge, its use as support has never been attempted for alkane oxidation. Moreover, although being known that salts of non-transition metals (e.g., Al [20], Ga, In [21] or Bi [22]) can catalyze alkane oxidation with hydrogen peroxide, the use of SnO<sub>2</sub> as catalyst for such oxidation has not been reported.

Aiming at the development of a more efficient and eco-friendly process for the synthesis of the industrially important KA oil, herein we report its successfully synthesis by oxidation of neat cyclohexane, with

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peroxide oxidants at room temperature (r.t.), catalyzed by Sn<sub>1</sub> –  $_x$ Co<sub>x</sub>O<sub>2</sub> –  $_\delta$  (x = 0, 0.01 or 0.05) nanoparticles (NPs). The NPs synthesis procedure and their structural, microstructural and optical characterization have been described elsewhere [23].

#### 2. Results and discussion

Fig. 1 shows a set of TEM and HRTEM micrographs of the undoped and Co-doped  $SnO_2$  nanopowders samples. As previously reported [23], all samples are composed of *quasi*-spherical single crystalline nanoparticles whose dimensions follow a lognormal distribution with mean grain sizes < 5 nm and the dopant element homogeneously distributed in the  $SnO_2$  matrix. In both undoped and Co-doped  $SnO_2$ HRTEM micrographs of Fig. 1, few nanoparticles showing the (110) planes are delimited by dotted circles stressing that nanoparticles are single crystalline domains.

The SnO<sub>2</sub>-based NPs can catalyze the oxidation of neat cyclohexane with a peroxide: hydrogen peroxide (aq., 30%), ter-butyl hydroperoxide (TBHP, aq. 70%), *m*-chloroperoxybenzoic acid (*m*CPBA, 77%) or urea hydrogen peroxide adduct (UHP) as depicted in Scheme 1. These new catalytic systems operate at room temperature and in solvent-free conditions. Cyclohexane is mainly oxidized to cyclohexyl hydroperoxide (CyOOH), cyclohexanol (CyOH) and cyclohexanone ( $Cy_{-H} = 0$ ). Precise quantification of the oxidation products present in the reaction mixture was performed by gas chromatography using Shul'pin's method [24-27] where cyclohexyl hydroperoxide was guantitatively converted to cyclohexanol by reduction with triphenylphosphine. The presence of the hydroperoxide was verified by additional GC injections of the samples before the treatment with triphenylphosphine (see experimental details in the electronic supplementary information (ESI)). Selected results corresponding to optimized experimental conditions (6 h reaction time, r.t.) are given in Table 1.

SnO<sub>2</sub>-based NPs act as highly selective catalysts towards the formation of cyclohexanol and cyclohexanone, since no traces of by-products were detected by GC–MS analysis of the final reaction mixtures for the optimized conditions (6 h reaction time, *see* Fig. S2 of ESI). However,



**Fig. 1.** TEM (up, left) and HRTEM (up, right) micrographs of undoped SnO<sub>2</sub> NPs. In the HRTEM micrograph four nanoparticles showing the (110) planes are delimited by dotted circles. The corresponding [110] directions are also given. HRTEM micrograph (down, left) of Sn<sub>0.95</sub>Co<sub>0.01</sub>O<sub>2</sub> –  $_{\delta}$  NPs and (down, right) HRTEM micrograph of Sn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>2</sub> –  $_{\delta}$  NPs. In both Co-doped SnO<sub>2</sub> micrographs few nanoparticles are delimited by dotted circles stressing that nanoparticles are single crystalline domains.

for longer reaction times (>6 h, *see* Fig. S2 of ESI) GC–MS analyses revealed the presence of 1,2- and 1,4-cyclohexanediol. This formation of side products of cyclohexane oxidation is believed to be the cause of KA oil yield decrease observed for such longer reactions times.

Experiments under N<sub>2</sub> atmosphere were also performed for the Sn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>2 -  $\delta$ </sub> nanocatalyst (Table 1, entry 13). The obtained overall yield and TON values are similar to that obtained in air (compare entries 9 and 13, Table 1), suggesting only a slightly promoting effect of the air atmosphere. Accordingly with less oxidant availability, the ratio cyclohexanol decreased.

Control experiments performed in the absence of the  $SnO_2$  NPs with any type of peroxide confirm the crucial role of the nanoparticles to efficiently catalyze the oxidation of cyclohexane (entries 17 to 20, Table 1). In fact,  $SnO_2$  NPs are believed to initially activate, not the alkane, but the oxidant (Eqs.1 and 2) and form oxygen-centered radicals that attack the alkane molecule generating the cyclohexyl radical Cy<sup>-</sup> (Eq. 3).

$$Sn^{4+}$$
 + 2 ROOH  $\rightarrow$  2 ROO<sup>-</sup> + 2 H<sup>+</sup> +  $Sn^{2+}$  (1)

$$Sn^{2+} + 2 ROOH \rightarrow 2 RO^{-} + Sn^{4+} + 2 HO^{-}$$
 (2)

$$RO' + CyH \rightarrow ROH + Cy'$$
 (3)

Cy<sup> $\cdot$ </sup>, in turn, reacts with dioxygen (Eq. 4) to form the cyclohexylperoxyl radical CyOO<sup> $\cdot$ </sup> which gives rise to the cyclohexyl hydroperoxide (CyOOH) (Eq. 5). The latter, in the presence of both reduced and oxidized forms of the SnO<sub>2</sub> nanocatalyst, decomposes (Eqs. 6–9) to cyclohexanone and/or cyclohexanol.

$$Cy^{\cdot} + O_2 \rightarrow CyOO^{\cdot} \tag{4}$$

$$CyOO^{\cdot} + ROOH \rightarrow CyOOH + ROO^{\cdot}$$
(5)

$$2 \text{ CyOOH} + \text{Sn}^{2+} \rightarrow 2 \text{ CyO}^{-} + 2 \text{ HO}^{-} + \text{Sn}^{4+}$$
(6)

2 CyOOH + Sn<sup>4+</sup> 
$$\rightarrow$$
 2 CyOO<sup>+</sup> + 2H<sup>+</sup> + Sn<sup>2+</sup> (7)

$$CyO' + CyH \rightarrow CyOH + Cy'$$
 (8)

2 
$$CyOO' + \rightarrow CyOH + Cy_{-H} = O + O_2$$
 (9)

The strong inhibition effect (drop over 90%, entries 11 and 12, Table 1) observed when the reaction was carried out in the presence of either the oxygen-radical trap  $Ph_2NH$  or the carbon-radical trap  $CBrCl_3$ , as well as the involvement of the hydroperoxide CyOOH in the catalytic reaction (compare entries 9 and 10, Table 1) suggests the involvement of the above radical mechanism for the cyclohexane oxidation catalyzed by the  $SnO_2$  NPs.

A maximum 15% yield of KA oil is achieved after 6 h reaction by using TBHP oxidant and SnO<sub>2</sub> nanopowder catalyst, with a turnover number (TON, moles products/mol nanocatalyst) of  $1.1 \times 10^3$  (see entry 1, Table 1). This is a marked improved catalytic activity relative to other nanocatalytic cyclohexane oxidation systems such as gold NPs supported at carbon nanotubes (3.6% maximum yield, TON of 43 [28]).

The use of other peroxides in the present protocol leads to lower yield and TON values (Table 1), following the trend *m*CPBA >  $H_2O_2$  > UHP, as depicted in Fig. 2. This oxidant dependent behavior was also found for other catalytic systems such as gold nanoparticles deposited on oxide supports [29] or heterogenized metal complexes [30], with TBHP exhibiting the highest oxidation efficiency. Further, replacement of peroxides by dioxygen as oxidant agent was not well succeed, allowing only a maximum of 0.6% total oxygenates yield (TON of 43). Moreover, Co-doping of SnO<sub>2</sub> nanoparticles leads to higher KA oil yield and TON values, as Co/Sn ratio increases, up to 25% yield and TON of  $1.9 \times 10^3$  (for Sn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>2</sub> –  $_{\delta}$  and TBHP, entry 10, Table 1), following the above-mentioned trend in respect to the type of oxidant (Fig.



**Scheme 1.** Cyclohexane oxidation to KA oil catalyzed by  $Sn_1 - {}_xCo_xO_2 - {}_\delta (x = 0, 0.01 \text{ or } 0.05)$  nanoparticles.

2). Such higher catalytic activity of Co-doped SnO<sub>2</sub> NPs may be due to the availability of an additional metal center to decompose the peroxide (Eqs. 10 and 11) as well as to react with formed cyclohexyl hydroperoxide to yield the cyclohexyl-oxyl (CyO<sup>•</sup>) and -peroxyl (CyO<sup>•</sup>) radicals that lead to KA oil (Eqs. 12 and 13) formation.

$$\operatorname{Co}^{2+}$$
 + ROOH  $\rightarrow$  RO<sup>-</sup> + CO<sup>3+</sup> + HO<sup>-</sup> (10)

$$\operatorname{Co}^{3+}$$
 +  $\operatorname{ROOH} \rightarrow \operatorname{ROO}^{\cdot}$  +  $\operatorname{H}^{+}$  +  $\operatorname{Co}^{2+}$  (11)

 $CyOOH + Co^{2+} \rightarrow CyO^{\cdot} + HO^{-} + Co^{3+}$ (12)

$$CyOOH + Co^{3+} \rightarrow CyOO^{\cdot} + H^{+} + Co^{2+}$$
(13)

Acidic reaction conditions, although not crucial for  $Sn_1 - {}_xCo_xO_2 - {}_\delta$ NPs catalytic activity, can enhance the cyclohexane oxidation. Fig. S1 (ESI) shows the effect of nitric acid amount on the total (cyclohexanone and cyclohexanol) TON for the oxidation of cyclohexane with TBHP catalyzed by  $Sn_{0.95}Co_{0.05}O_{2-\delta}$ .NPs (*see* also Table S1 of ESI). The catalytic activity increases with the HNO<sub>3</sub> amount up to a maximum for the acidto-cyclohexane molar ratio of 0.3. This favorable effect of acid may be associated to hydrogen-transfer, namely promoting the formation of cyclohexyl-peroxyl (CyOO<sup>-</sup>) and -oxyl (CyO<sup>-</sup>) radicals [31]. Note

#### Table 1

Selected data<sup>a</sup> for the optimized oxidation of cyclohexane with peroxides, catalyzed by Sn<sub>1 - x</sub>Co<sub>x</sub>O<sub>2 -  $\delta$ </sub> (x = 0, 0.01 or 0.05) nanoparticles.

Entry	x	Oxidant	TON <sup>b</sup>	Yield <sup>d</sup> (%)		
			СуОН	$Cy_{-H} = 0$	Total <sup>c</sup>	
1	0	TBHP	632	489	1121	15.2
2		$H_2O_2$	53	33	86	1.2
3		UHP	49	27	76	1.0
4		m-CPBA	202	106	308	4.2
5	0.01	TBHP	859	507	1366	18.5
6		$H_2O_2$	299	110	409	5.5
7		UHP	123	77	200	2.7
8		m-CPBA	266	232	498	6.7
9	0.05	TBHP	1490	380	1870	25.2
10 <sup>e</sup>			673	421	1094	15.3
11 <sup>f</sup>			127	60	187	2.5
12 <sup>g</sup>			101	50	151	2.0
13 <sup>h</sup>			1459	248	1707	23.9
14		$H_2O_2$	320	110	430	5.8
15		UHP	118	93	211	2.9
16		m-CPBA	380	180	560	7.6
17	no catalyst	TBHP	-	-	-	0.3
18		$H_2O_2$	-	-	-	0.0
19		UHP	-	-	-	0.0
20		m-CPBA	-	-	-	0.1

 $^a~$  Reaction conditions:  $C_6H_{12}~(5~mmol),$  nanocatalyst (0.7  $\mu mol,$  0.014 mol% vs. substrate), r.t. 6 h.

<sup>b</sup> Turnover number (moles of product per mol of nanocatalyst).

<sup>c</sup> Cyclohexanol + cyclohexanone.

<sup>d</sup> Amount of cyclohexanone and cyclohexanol determined after reduction of the aliquots with solid PPh<sub>3</sub> using cycloheptanone as standard.

<sup>e</sup> Without treatment of PPh<sub>3</sub>.

<sup>f</sup> In the presence of CBrCl<sub>3</sub>.

<sup>g</sup> In the presence of Ph<sub>2</sub>NH.

h Under N2 atmosphere.

however that a further increase of the HNO<sub>3</sub> amount results in a decreasing of the catalytic activity, which may be due to the competition between the cyclohexane, the oxidant and the acid for the active sites at the surface of the  $Sn_1 - xCo_xO_2 - \delta$  NPs [32,33].

The present Co-doped SnO<sub>2</sub> nanopowders/TBHP/r.t. systems exhibit improved catalytic efficiency relative to other Co containing catalytic cyclohexane oxidation heterogeneous systems such as Co-doped SAPO-5 molecular sieves (selective conversion of cyclohexane to KA oil up to 6.30%) [34] or Mn-Co mixed oxides (Mn<sub>a</sub>Co<sub>b</sub>O<sub>x</sub>) catalysts (up to 10.4% conversion of cyclohexane and 62.0% selectivity) [35] using molecular oxygen as oxidant at 140 °C.

The Sn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>2 –  $\delta$ </sub> nanocatalyst, in the presence of hydrogen peroxide or TBHP, maintains its catalytic efficiency to produce KA oil during five consecutive cycles and retained its initial activity over ~90% as well as its selectivity. Moreover, the XRD patterns of the nanocatalyst show that its crystallographic structure is kept after the 5 catalytic cycles, as can be seen in Fig. 3. Indeed, the diffractograms of both as-prepared and reused NPs show broad peaks matching the expected diffraction reflections of the (110), (101), (200), (211) and (220) rutile SnO<sub>2</sub> planes, according to the JCPDS file 41-1445 [36]. These results seem to support that Sn<sub>1</sub> –  $_x$ Co<sub>x</sub>O<sub>2</sub> –  $_\delta$  behave as a truly nanocatalyst during the cyclohexane oxidation.

The catalytic applicability of  $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$  NPs was extended. Other cycloalkanes, namely cyclopentane and -heptane were selectively converted in the corresponding alcohols and ketones, although in lower yields (*see* Table 2). The activity trend of the NPs observed for cyclohexane was maintained. The lower conversion of cyclo-pentane and -heptane into the corresponding alcohols and ketones could be related with the ring strain (ca. 6.5 kcal mol<sup>-1</sup>) exhibited by both cycloalkanes which decreases the stability of their rings in comparison with the 6-membered ring (ring strain of 0 kcal mol<sup>-1</sup>). In fact, GC–MS analysis of the final reaction mixtures from the above conditions revealed a significant presence of "overoxidation" products such as the corresponding



**Fig. 2.** Effect of type of oxidant on the total yield for the peroxidative oxidation of cyclohexane catalyzed by the different  $\text{Sn}_{1 - x}\text{Co}_x\text{O}_{2 - \delta}$  nanoparticles: x = 0 (), 0.01 () and 0.05().



**Fig. 3.** XRD patterns of the  $Sn_{0.95}Co_{0.05}O_2 - \delta$  nanocatalyst as-prepared (——) and after 5 catalytic cycles of cyclohexane oxidation using TBHP (——) or  $H_2O_2$  (——) as oxidant. Labelled crystallographic planes were taken from the SnO<sub>2</sub> JCPDS file no. 41-1445 [36].

cycloalkanediols and carboxylic acids. A better understanding of the optimal conditions for the catalytic systems with these substrates seems to be worthy of further development, a topic that will be addressed in future studies.

#### 3. Conclusions

 $Sn_{1-x}Co_xO_{2-\delta}$  (x = 0, 0.01 or 0.05) nanoparticles with mean grain sizes < 5 nm were successfully used as catalysts for the oxidation of cyclohexane leading to KA oil, in the presence of peroxides at room temperature and in solvent-free medium. Our results indicated that  $SnO_2$ -based nanoparticles were very active for the synthesis of cyclohexanol and cyclohexanone, and no traces of by-products were detected under optimized conditions. The best catalytic performance was achieved for the  $Sn_{1-x}Co_xO_{2-\delta}$  NPs with a Co/Sn ratio of 5%, using TBHP as oxidant in acidic medium.

The recyclability of the Sn<sub>0.95</sub>Co<sub>0.05</sub>O<sub>2</sub> –  $_{\delta}$  nanocatalyst was also studied and it was concluded that the NPs are easily recovered and reused, their catalytic activity remaining almost constant after five reaction cycles while maintaining selectivity.

These results have an important implication on the design of SnO<sub>2</sub>based alkane oxidation nanocatalysts and are of potential significance for the industrial production of KA oil.

#### Table 2

Selected data<sup>a</sup> for the optimized oxidation of cyclopentane and cycloheptane with TBHP, catalyzed by Sn<sub>1</sub> –  $_x$ Co<sub>x</sub>O<sub>2</sub> –  $_{\delta}$  (x = 0, 0.01 or 0.05) NPs.

Entry	x	Substrate	TON <sup>b</sup>			Yield <sup>d</sup> (%)
			ROH	$R_{-H} = O$	Total <sup>c</sup>	
1	0	C <sub>5</sub> H <sub>10</sub>	30	19	49	0.7
2		C7H14	556	55	611	8.6
3	0.01	C <sub>5</sub> H <sub>10</sub>	46	25	71	1.0
4		C7H14	608	53	661	9.3
5	0.05	C5H10	59	21	80	1.1
6		C7H14	673	67	740	10.4

 $^a\;$  Reaction conditions:  $C_5H_{10}$  or  $C_7H_{14}$  (5 mmol), TBHP (10 mmol), nanocatalyst (0.7  $\mu$ mol, 0.014 mol% vs. substrate), r.t., 6 h.

<sup>b</sup> Turnover number (moles of product per mol of nanocatalyst).

 $^{c}$  R<sub>-H</sub> = O + ROH (R = C<sub>5</sub>H<sub>9</sub> or C<sub>7</sub>H<sub>13</sub>).

 $^d\,$  Amount of  $R_{\cdot H}=0$  and ROH  $(R=C_5H_9$  or  $C_7H_{13})$  determined after reduction of the aliquots with solid PPh\_3.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2017.03.012.

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