Research Article

Effect of Pr, Sm, and Tb Doping on the Morphology, Crystallite Size, and N\textsubscript{2}O Decomposition Activity of Co\textsubscript{3}O\textsubscript{4} Nanorods

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Cobalt(II,III) oxide, Co\textsubscript{3}O\textsubscript{4}, is a promising catalyst for nitrous oxide direct decomposition. In this paper we report effect of doping with some rare earth (RE) elements (Pr, Sm, and Tb) on the morphology and crystallite size of Co\textsubscript{3}O\textsubscript{4} nanorods. The various precursors (RE/Co oxalates) were prepared via the microwave assisted method and subsequent calcination. The decomposition pathway of these precursors was followed using thermogravimetric analysis (TGA). Based on thermal analysis results, Pr-, Sm-, and Tb-doped Co\textsubscript{3}O\textsubscript{4} samples were obtained via the calcination in static air at 500°C for their oxalate precursors. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and hydrogen temperature programmed reduction (H\textsubscript{2}-TPR) were used to characterize the RE-doped cobalt oxide catalysts. The activity of the prepared catalysts was investigated for N\textsubscript{2}O direct decomposition and compared with that of the undoped Co\textsubscript{3}O\textsubscript{4} catalyst. It was shown that the promoted Co\textsubscript{3}O\textsubscript{4} catalysts revealed higher activity compared to the unpromoted one. The dependence of the activity on both the catalysts particle size and the reduction behaviour was discussed.

1. Introduction

Due to the unawareness of its harmful effects nitrous oxide (N\textsubscript{2}O) has suffered, for a long time, from the lack of interest from the environmental scientists [1, 2]. Only during the last two decades a growing interest can be noticed with N\textsubscript{2}O abatement studies. This is especially after its citation as a second non-CO\textsubscript{2} greenhouse gas. Moreover, it was recognized that it causes the destruction of ozone in the stratosphere and it causes the acid rains. Due to its long lifetime, about 150 years, N\textsubscript{2}O has a Global Warming Potential (GWP) of 310 and 21 times that of CO\textsubscript{2} and CH\textsubscript{4}, respectively [1, 2]. The industrial processes that involve N\textsubscript{2}O emission include adipic acid, nitric acid, caprolactam, acrylonitrile, and glyoxal manufactures. Moreover, N\textsubscript{2}O is emitted as a byproduct of some processes like the nonselective catalytic reduction of NO (NSCR) with cyanuric acid or urea and in three-way catalysis (TWC) to remove NO, CO, and hydrocarbons [1, 2].

Accordingly, N\textsubscript{2}O was cited as the second non-CO\textsubscript{2} greenhouse gas Kyoto Protocol of the United Nations Convention on Climate Change (December 1997). Based on that protocol the industrial countries should reduce their collective greenhouse gas (GHG) emissions by values slightly higher than 5% below their 1990 values [1, 2]. On the other hand, the developed countries have to reduce their GHG emissions by values around 5%. Such targets will be increased in the next protocol of the United Nations that will replace the Kyoto protocol. The catalytic routes represent the most important and applied solutions for this environmental problem. Among them the direct decomposition of nitrous oxide to its elements, that is, nitrogen and oxygen, is considered to be a simple and effective way to minimize the N\textsubscript{2}O...
emissions. Many catalysts categories have been developed for N$_2$O decomposition.

Cobalt(II,III) oxide, Co$_3$O$_4$, is a black antiferromagnetic solid, $\beta$-type semiconductor and has direct optical band gap at 2.18–3.52 eV [3]. Co$_3$O$_4$ adopts the normal spinel structure, represented as AB$_2$O$_4$ in which A ions, Co$_{2+}$ (3d$^9$), occupying tetrahedral sites and B ions, Co$_{3+}$ (3d$^8$), are located in octahedral sites. Co$_3$O$_4$ has been investigated extensively as promising catalysts for N$_2$O direct decomposition [4–14].

Russo et al. [4] have checked the activity of three series of metal (Mg, Ca, Mn, Co, Ni, Cu, Cr, Fe, and Z) spinels (cobaltites, chromites, and ferrites) prepared by the solution combustion method. Their results demonstrated that among the categories the cobalt containing spinels exhibit the best activity. Moreover, MgCo$_2$O$_4$ showed the best performance among the different metal cobaltites in the absence and presence of oxygen. This was attributed to its higher concentration of suprafacial-weakly chemisorbed oxygen species. Over a series of $M_xCo_{1-x}O_4$ (M = Mg, Ni, Zn, $x =$ 0.0–0.99) spinel catalysts, prepared by the coprecipitation method, Yan et al. [5, 6] found that the N$_2$O decomposition activity depends on the degree of Co$_{2+}$ substitution by Mg$_{2+}$ or Ni$_{2+}$ or Zn$_{2+}$. The highest activities were observed over Mg$_{85.5}$Co$_{14.5}$O$_4$, Ni$_{80}$Zn$_{20}$O$_4$, and Zn$_{36}$Co$_{64}$O$_4$ catalysts. Concurrently, for Cu$_x$Co$_{1-x}$O$_4$ and Ni$_x$Co$_{1-x}$O$_4$ catalysts (0.0 $\leq$ $x$ $\leq$ 1.0) spinel-oxide catalysts, prepared via the coprecipitation method, it was found that the highest activity was exhibited by the catalysts 0.75 and 0.50, respectively [7, 8]. Moreover, increasing the calcination temperature till 900°C for both series was accompanied by a sharp activity decrease. The activity of Mg$_{0.9}$Co$_{0.1}$O$_4$ (0.0 $\leq$ $x$ $\leq$ 1.0) catalysts, prepared by the impregnation method, was found to increase the $x$-value [9].

With respect to the influence of promoters, Xue et al. reported a beneficial effect on doping Co$_3$O$_4$ spinel with ceria [10]. On varying the Ce/Co molar ratio, a complete N$_2$O conversion below 400°C was obtained for the catalyst having a ratio of 0.05. The promotion effect was attributed to the role of CeO$_2$ in promoting the reduction of Co$_{3+}$ to Co$_{2+}$, thus facilitating the desorption of adsorbed oxygen species, which is deemed to be the rate-determining step for N$_2$O decomposition. The activity of cobalt containing spinels was also markedly enhanced by doping with alkali cations. In this regard, the presence of residual K ions has led to an activity enhancement for Co$_3$O$_4$-CeO$_2$ (Ce/Co = 0.05) catalyst [11]. Potassium and cesium ions were found to be superior to lithium and sodium ones [9]. Recently, an activity enhancement was reported by the addition of K ions to Zn$_{0.5}$Co$_{0.5}$O$_4$ [12], MgCo$_2$O$_4$ [9], and Co$_3$O$_4$ [13] catalysts. Doping with alkali earth cations was also reported to improve the activity of spinel oxide catalysts. In this context, N$_2$O decomposition over a series of MCO$_2$-Co$_3$O$_4$ (M = Ca, Sr, Ba) catalysts having M/Co ratios of 0.1–0.4 revealed that the catalysts containing Sr and Ba ions exhibit the highest activity [14]. The crystallite size and the calcination temperature are other factors that influence the N$_2$O decomposition of the oxide spinel catalysts; lower values of both factors increase the catalytic activity [7–9, 14].

The previous literature data reveals that the activity of Co$_3$O$_4$ spinel oxide-based catalysts is sensitive to the preparation method, the degree of Co$_{2+}$ substitution, the calcination temperature, crystallite size, and presence of dopants. The role of rare earth oxides as promoters during N$_2$O direct decomposition was reported for some catalytic systems. For instance, Bueno-López et al. [15] demonstrated that the addition of La, Pr dopants increases the activity of Rh/Co$_3$O$_4$ catalysts markedly. This was attributed to the role of the added RE cation in stabilizing the catalysts active phase (Rh$_2$O$_3$). Synergic catalytic performance compared to the single oxides was reported for CuO/Co$_3$O$_4$ catalysts [16]. This effect was related to the enhanced catalysts reducibility as well as the facile Ce$^{4+}/$Ce$^{3+}$ and Cu$^{2+}/$Cu$^+$ redox cycles. Concurrently, Konsolakis et al. [17] reported a dramatic enhancement of de-N$_2$O performance of Pr/Al$_2$O$_3$ by the incorporation of 20 wt% CeO$_2$-La$_2$O$_3$ mixed oxide on the Al$_2$O$_3$ support. To the best of our knowledge, there are limited reports concerning the influence of the rare earth oxides dopants on the N$_2$O decomposition activity of Co$_3$O$_4$ spinel oxide catalyst. Therefore, based on the expected promotion effect of the RE dopants as it was reported for other catalysts, in this paper we report the enhancement effect of doping Co$_3$O$_4$ with some rare earth (RE) elements (Pr, Sm, and Tb) during N$_2$O direct decomposition. The examined catalysts were prepared via the microwave assisted method of cobalt oxalate and subsequent calcination. Special focus will be given to the catalysts characterization in order to check the influence of the added RE elements on the morphology and crystallite size of Co$_3$O$_4$ nanorods.

2. Materials and Methods

2.1. Catalysts Preparation. Cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O), praseodymium nitrate (Pr(NO$_3$)$_3$·6H$_2$O), samarium nitrate (Sm(NO$_3$)$_3$·6H$_2$O), terbium nitrate (Tb(NO$_3$)$_3$·6H$_2$O), oxalic acid (H$_2$C$_2$O$_4$), and cetyltrimethylammonium bromide (CTAB) are of analytical grade and were used as received without further purification. Co$_3$O$_4$ was prepared by microwave assisted precipitation method (in the form of cobalt oxalate) using a microwave power of 560 W and subsequent calcination at 500°C. Detailed information about the preparation procedure is given elsewhere [18]. The rare earth-promoted Co$_3$O$_4$ catalysts were prepared employing the coprecipitation method. In this method the amount of a rare earth cation (Pr$^{3+}$, Sm$^{3+}$, and Tb$^{3+}$), required to achieve rare earth (RE)/Co ratio of 0.05, was added during the precipitation of cobalt oxalate using the same working procedure. After drying the coprecipitated oxalates, they were calcined for 1 h at 500°C in air to yield the corresponding earth-promoted Co$_3$O$_4$ catalysts. Scheme 1 shows an illustration and mechanism of the Co$_3$O$_4$ and RE/Co$_3$O$_4$ catalyst synthesis.

2.2. Characterization Techniques. TGA and DTG curves were recorded with the aid of TA instrument apparatus (model TGA-Q500) using a heating rate of 10°C min$^{-1}$ and an average sample weight of 5 mg in nitrogen flow.
2.3. Activity Measurements. The catalytic tests were carried out in a fixed-bed quartz-glass flow reactor, at atmospheric pressure, containing approximately 0.5 g of the catalyst. The experiments were carried out at the temperature range of 150–500°C and a W/F value of 0.15 g s cm⁻³. The N₂O gas was introduced onto the catalyst bed from the bottom. The reactor was heated using a temperature-controlled furnace. The temperature in the reactor was measured using a thermocouple on the catalyst bed. Prior to the reaction all the catalysts were pretreated for 1 h in helium at 500°C. The reactant gas, 500 ppm N₂O, was introduced to the catalyst bed with the aid of Bronkhorst thermal mass flow controllers using helium as a balance gas. The N₂O concentrations in the inlet and outlet streams were measured using nondispersive infrared analyser (Hartmann and Braun, Uras 10E).

3. Results and Discussion

3.1. Catalysts Characterization. As it was mentioned in the introduction that the calcination temperature has a crucial effect on the catalytic behaviour of the Co₃O₄-based catalysts, therefore, in order to identify the appropriate calcination temperature of the parent cobalt oxalate and its RE-containing mixtures, the thermal stability of these parents has been checked by TGA during the heating up to 700°C. Our more recent work demonstrated that the preparation procedure followed has led to the formation of cobalt oxalate with the formula CoC₂O₄·2H₂O [18]. The obtained TGA-DTG curves are shown in Figure 1. Two weight loss (WL) events can be observed for the undoped cobalt oxalate (Figure 1(a)). These events are accompanied by WL values of 19.58 and 46.11% and are maximized at 162 and 366°C. The first WL agrees well with that (19.69%) expected for the dehydration of the parent CoC₂O₄·2H₂O. The obtained second WL% is higher than that expected for the formation of Co₃O₄ (36.44%) or CoO (39.36%) and lower than that anticipated for the formation of metallic Co (48.10%). This suggests that the residue formed in the second step is composed mainly of metallic cobalt. In agreement, Deng et al. [19] reported the formation of β-Co as a result of the thermal decomposition of its β-CoC₂O₄·2H₂O precursor in N₂ flow at 395°C. In this context, it is to be mentioned that conducting the experiment air flow has led to the formation of Co₃O₄ as a second decomposition step product [18–20]. The TGA thermograms obtained for the RE/cobalt oxalate mixtures (Figures 1(b)–1(d)) reveal the emergence of an early WL step (maximized at the temperature range of 54–86°C). This step could be related to the dehydration of the RE oxalates. Meanwhile, two other peaks can be observed in the three thermograms, which are maximized at the temperature ranges of 162–170°C and 366–372°C. No other WL steps can be observed in the three thermograms. Therefore, it is plausible to assign the former set of peaks to the dehydration of cobalt oxalate, whereas the second set of peaks is assigned to the decomposition of the anhydrous RE/cobalt oxalates. TGA curve of the Tb/Co mixture indicates the presence of a mild-gradual weight gain at temperatures higher than 425°C. This weight gain could be related to the oxidation of the obtained metallic cobalt by the traced amount of oxygen in the flow. According to the TGA results the various parents were calcined at 500°C for 1 h in order to obtain the relevant nanocrystalline Co₃O₄-based catalysts.

Figure 2 shows the XRD patterns of the calcined cobalt oxalate and its RE-containing mixtures. XRD pattern for the undoped Co₃O₄ catalyst (Figure 2(a)) reveals that the presence of reflections matches well with those of the cubic
Co$_3$O$_4$ spinel oxide (space group Fd3m; JCPDS card number 42-1467) [18, 20–26]. No other peaks assignable to Co$_3$O$_4$, CoO, and Co were detected indicating that the decomposition of cobalt oxalate in air proceeds with the formation of Co$_3$O$_4$ spinel oxide as a pure phase. The XRD pattern of the Pr containing catalyst (Figure 2(b)) reveals the presence of reflections due to the Co$_3$O$_4$ phase (JCPDS card number 42-1121). This indicates that this catalyst is composed of Co$_3$O$_4$, and terbium/cobalt oxalates (c), and praseodymium/cobalt oxalates (b), samarium/cobalt oxalates (c), and terbium/cobalt (d) oxalates till 700°C. The diffractogram of the Tb/Co catalyst (Figure 2(d)) reveals the presence of other weak absorptions at the wavenumber range of 1700–1200 cm$^{-1}$, which can be assigned to the presence of surface carbonate species [7, 8, 14]. This indicates the ability of the added RE oxides to form weak surface carbonates upon contact with atmospheric air.

Figure 4 shows the SEM images of the neat Co$_3$O$_4$ as well as its Pr, Sm, and Tb containing catalysts prepared by the coprecipitation method and calcined at 500°C. It is evident that the neat Co$_3$O$_4$ (Figure 4(a)) consists of sets of rods. Adding the RE oxides to Co$_3$O$_4$ resulted in dramatic morphological changes. The Pr$_6$O$_{11}$/Co$_3$O$_4$ catalyst (Figure 4(b)) consists of network polygons within the frame of spheres agglomerations. The Sm$_2$O$_3$/Co$_3$O$_4$ (Figure 4(c))
Figure 2: XRD patterns of Co₃O₄ (a) catalyst and its Pr (b), Sm (c), and Tb (d) containing catalysts being prepared by the impregnation method at RE/Co ratio of 0.05 and calcined at 500°C.

Figure 3: FTIR spectra of Co₃O₄ (a) catalyst and its Pr (b), Sm (c), and Tb (d) containing catalysts being prepared by the impregnation method at RE/Co ratio of 0.05 and calcined at 500°C.
Figure 4: SEM images of as-prepared Co$_3$O$_4$ (a), Pr$_6$O$_{11}$/Co$_3$O$_4$ (b), Sm$_2$O$_3$/Co$_3$O$_4$ (c), and Tb$_4$O$_7$/Co$_3$O$_4$ (d) being prepared by the coprecipitation method and calcined at 500°C.

consists of sets of welded rods which have smaller dimensions than those of the neat Co$_3$O$_4$. Finally, the Tb$_4$O$_7$/Co$_3$O$_4$ catalyst (Figure 4(d)) shows agglomeration of polydisperse rectangles.

The TEM images of the neat Co$_3$O$_4$ as well as its Pr, Sm, and Tb containing catalysts prepared by the coprecipitation method and calcined at 500°C are depicted in Figure 5. One can clearly show that rod morphology of the unpromoted Co$_3$O$_4$ (Figure 5(a)) is composed of sets of capsules having diameters in the range of 35–65 nm and lengths of 50–180 nm. These rods are welded to form larger ones. The Pr$_6$O$_{11}$/Co$_3$O$_4$ catalyst (Figure 5(b)) shows irregular shape particles having diameters in the range of 15–50 nm. Similar morphology can be seen for the Sm$_2$O$_3$/Co$_3$O$_4$ catalyst (Figure 5(c)) with particles diameters in the range of 20–60 nm. The Tb$_4$O$_7$/Co$_3$O$_4$ catalyst (Figure 5(d)) shows irregular shaped agglomerations of particles with dimensions in the range of 20–100 nm. Thus, the electron microscopic examination reveals that the rod-like morphology of Co$_3$O$_4$ is very sensitive to the presence of these RE oxides. The presence of such dopants even in small concentration is sufficient to destroy this rod-like morphology.

3.2. Catalytic Activity Measurements. The activity of the three RE-promoted Co$_3$O$_4$ catalysts was tested for N$_2$O decomposition and compared with that of the unpromoted Co$_3$O$_4$. Figure 6 shows the dependence of N$_2$O conversion percentage on the reactor temperature for these series of catalysts being prepared by the coprecipitation method. One can easily spot the fact that the activity increases continuously with the reactor temperature over all the tested catalysts. Moreover, all the RE containing catalysts showed higher N$_2$O decomposition activity compared to the bare Co$_3$O$_4$ catalyst. In the open literature, there are many papers reporting the promotion effect of various promoters during N$_2$O decomposition over Co$_3$O$_4$-based catalysts. For instance, partial substitution of Co$^{2+}$ ions in Co$_3$O$_4$ spinel oxide with various metal ions (Mg$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$) has led to a noticeable increasing of its activity [5–9]. Activity enhancement was also observed on doping Co$_3$O$_4$-based catalysts with some promoters like ceria [10], zirconia [28], alkali [11–13, 29, 30], and alkali-earth [14] cations. In some of these papers the enhanced N$_2$O decomposition activity was correlated with the Co$_3$O$_4$ crystallite size [7–9, 14], where high activity was observed over small Co$_3$O$_4$ crystallite size. Concurrently, an inverse relationship between the Ag$^{0}$ crystallites size and the N$_2$O conversion % was reported for Ag/Fe$_2$Al$_{2-x}$O$_3$ catalysts [31]. Similarly, the higher N$_2$O decomposition activity of the RE/Co$_3$O$_4$ catalysts compared to that of the bare Co$_3$O$_4$ one could be related to the induced Co$_3$O$_4$ crystallite size reduction by the added RE ions as it was observed during the TEM analysis (Figure 5).

The reported reaction mechanism of the N$_2$O decomposition over Co$_3$O$_4$-based catalysts involves electron donation...
Figure 5: TEM images of as-prepared Co$_3$O$_4$ (a), Pr$_6$O$_{11}$/Co$_3$O$_4$ (b), Sm$_2$O$_3$/Co$_3$O$_4$ (c), and Tb$_4$O$_7$/Co$_3$O$_4$ (d) being prepared by the coprecipitation method and calcined at 500°C.

from an active center at the catalyst surface, which is a metal ion in a low oxidation state (probably Co$^{2+}$), to the N$_2$O molecule as follows [9, 14, 28]:
\[
N_2O(g) + Co^{2+} \rightarrow N_2O^-(ads) \cdots Co^{3+}
\]
This step is accompanied by Co$^{2+}$ oxidation to Co$^{3+}$ together with the formation of one N$_2$ molecule and a chemisorbed oxygen atom. Thus, the recoverability of Co$^{2+}$ is crucial for attaining high N$_2$O decomposition activity as shown in (3). One has
\[
N_2O^-(ads) \cdots Co^{3+} \rightarrow N_2(g) + O^-(ads) \cdots Co^{3+}
\]
\[
O^-(ads) \cdots Co^{3+} \rightarrow \frac{1}{2} O_2(g) + Co^{2+}
\]
Therefore, H$_2$-TPR measurements were performed in order to examine the effect of the addition of RE ions on the reduction behaviour of Co$_3$O$_4$ spinel oxide. The obtained TPR curves of these catalysts are depicted in Figure 7. All the TPR profiles in Figure 7 reveal the existence of one broad peak, which extends over the temperature range of 280–520°C. This finding indicates that this peak could describe several overlapping reduction processes. In agreement with other literature data, such peak could be assigned to the reduction of Co$^{3+}$ to Co$^{2+}$ and Co$^{2+}$ to Co$^{0}$ according to [10, 32]:
\[
Co_3O_4 + H_2 \rightarrow 3CoO + H_2O
\]
\[
3CoO + 3H_2 \rightarrow 3Co + 3H_2O
\]
The obtained TPR profiles indicate that the reduction behaviour of Co$_3$O$_4$ is greatly influenced by the added RE oxides. $T_{max}$ of the reduction peak is shifted from 448°C for Co$_3$O$_4$ to 441, 435, and 431°C for Pr-, Sm-, and Tb-promoted Co$_3$O$_4$, respectively. Moreover, the onset temperature of the reduction is shifted towards lower temperatures for the RE-promoted Co$_3$O$_4$ compared to the unpromoted one. These findings, in turn, suggest that the reduction behaviour of Co$_3$O$_4$ is enhanced by the addition of the RE oxides.

More recently, it was demonstrated that the fine tuning of Cu facilitates the reduction of Co$^{3+}$ and Co$^{2+}$ in Cu$_x$Co$_{3−x}$O$_4$ spinel [33]. This promotion of the catalysts reducibility was correlated with the increase in the N$_2$O direct decomposition over this series of catalysts. For a series of Ce-doped Co$_3$O$_4$ catalysts, Xue et al. [10, 11] showed that the reduction behaviour of these catalysts is influenced by the Ce/Co ratio as well as the preparation method. They concluded that the higher the Co$^{3+}$ reducibility of the Co$_3$O$_4$-CeO$_2$ catalyst, the higher the N$_2$O decomposition activity.
Chromčíková et al. [32] reported a direct dependence of the reduction ability and the catalytic behaviour during N₂O direct decomposition of a series of Co₃O₄ catalysts prepared via different routes. The results of N₂O decomposition over bare Pr₆O₁₁, Sm₂O₃, and Tb₂O₇ (not shown) revealed that these oxides exhibit very low activities (less than 5% conversion at 500 °C). This finding suggests that the active catalysts centers could be Co²⁺→Co³⁺ redox pair. And based on the H₂-TPR results, we can confidently state that the improved reducibility of the Co³⁺ to Co²⁺, induced by the incorporation of RE oxides into Co₃O₄, could be an additional factor for their higher N₂O decomposition activity compared to that of the unpromoted Co₃O₄. Accordingly, the reaction mechanism can be understood as follows: as the reaction proceeds N₂O is adsorbed on an active catalyst center (Co²⁺) as indicated by (1). This step is followed by the liberation of one nitrogen molecule leaving back and adsorbed oxygen atom over a catalyst center with higher oxidation state, that is, Co³⁺. The addition of the RE oxides to improve the reducibility of the catalyst, that is, enhances the recoverability of the catalyst active center (Co³⁺) as indicated by (3).

4. Conclusions

Series of RE-doped Co₃O₄ precursors were prepared by the microwave assisted method employing oxalic acid as precipitating agent. The RE-doped Co₃O₄ catalysts were obtained by the calcination, in air at 500°C, of these precursors. The obtained catalysts were characterized using XRD, FT-IR, SEM, TEM, and H₂-TPR techniques and tested for N₂O direct decomposition. It was found that the addition of the RE oxides to the Co₃O₄ spinel enhances its N₂O decomposition activity. The superior activity of the RE-promoted Co₃O₄ catalysts to that of the unpromoted Co₃O₄ one was correlated with the observed decrease in the particle size of Co₃O₄ as well as the facilitated Co³⁺→Co²⁺ reduction.
Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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