Comparison of Different Metal Doping Effects on \( \text{Co}_3\text{O}_4 \) Catalysts for the Total Oxidation of Toluene and Propane

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**Abstract:** Metal-doped (Mn, Cu, Ni, and Fe) cobalt oxides were prepared by a coprecipitation method and were used as catalysts for the total oxidation of toluene and propane. The metal-doped catalysts displayed the same cubic spinel \( \text{Co}_3\text{O}_4 \) structure as the pure cobalt oxide did; the variation of cell parameter demonstrated the incorporation of dopants into the cobalt oxide lattice. FTIR spectra revealed the segregation of manganese oxide and iron oxide. The addition of dopant greatly influenced the crystallite size, strain, specific surface area, reducibility, and subsequently the catalytic performance of cobalt oxides. The catalytic activity of new materials was closely related to the nature of the dopant and the type of hydrocarbons. The doping of Mn, Ni, and Cu favored the combustion of toluene, with the Mn-doped one being the most active \((14.6 \times 10^{-8} \text{ mol g}_{\text{Co}}^{-1} \text{ s}^{-1} \text{ at } 210 \degree \text{C}; T_{50} = 224 \degree \text{C})\), while the presence of Fe in \( \text{Co}_3\text{O}_4 \) inhibited its toluene activity. Regarding the combustion of propane, the introduction of Cu, Ni, and Fe had a negative effect on propane oxidation, while the presence of Mn in \( \text{Co}_3\text{O}_4 \) maintained its propane activity \((6.1 \times 10^{-8} \text{ mol g}_{\text{Co}}^{-1} \text{ s}^{-1} \text{ at } 160 \degree \text{C}; T_{50} = 201 \degree \text{C})\). The excellent performance of Mn-doped \( \text{Co}_3\text{O}_4 \) could be attributed to the small grain size, high degree of strain, high surface area, and strong interaction between Mn and Co. Moreover, the presence of 4.4 vol.% \( \text{H}_2\text{O} \) badly suppressed the activity of metal-doped catalysts for propane oxidation, among them, Fe-doped \( \text{Co}_3\text{O}_4 \) showed the best durability for wet propane combustion.

**Keywords:** metal doping; cobalt oxide; synergistic effect; VOC oxidation; toluene; propane

1. Introduction

Hydrocarbons emitted from both industrial manufacture and motor vehicle exhaust cause a lot of atmospheric pollution. Catalytic combustion is one of the most promising countermeasures for the elimination of hydrocarbons. As an inexpensive and active catalyst, \( \text{Co}_3\text{O}_4 \) has attracted much interest in the past decade as a substitute for the noble metal catalysts.

Liu et al. prepared nanocrystalline cobalt oxide by a soft reactive grinding procedure, the catalyst shows high specific rate for propane total oxidation benefiting from a high concentration of superficial electrophilic oxygen (O\(^-\)) species [1]. Garcia et al. synthesized ordered \( \text{Co}_3\text{O}_4 \) via a nanocasting method using KIT-6 as the hard template. The good activity of these catalysts in the total oxidation of toluene and propane was correlated with both the high surface area and the presence of oxygen vacancies instead of the ordered structure [2]. Marin et al. produced very active \( \text{Co}_3\text{O}_4 \) catalyst with...
50% propane conversion at 175 °C using a supercritical CO2 anti-solvent precipitation method [3]. Salek et al. obtained Co3O4 with high porosity by moderate calcination of CoO(OH) derived from aqueous precipitation. This catalyst showed a superior activity for CO and propane total oxidation [4]. By using an acetic acid leaching strategy, Tang and his co-workers modified the surface structure and chemistry of Co3O4 nanoparticles and obtained a Co3O4 catalyst with more abundant defects, surface Co2+, and chemisorbed oxygen species, which presented a much higher activity than the commercial Pt/Al2O3 and Pd/Al2O3 catalysts [5]. Analogously, Li et al. fabricated mesoporous Co3O4 via nitric acid treatment, and the as-prepared catalyst showed enhanced activity in toluene oxidation due to higher specific surface areas, more weak acidic sites, and a greater amount of surface Co2+ and adsorbed oxygen species [6]. Ren et al. constructed various 3D hierarchical Co3O4 nanocatalysts via a hydrothermal process and demonstrated that the hierarchical cube-stacked Co3O4 microspheres exhibited best activity for toluene oxidation [7]. Nevertheless, it is still a challenge to increase the catalytic activity of Co3O4 for different VOCs to broaden the feasible range and meet the need of realistic application.

Substituting a small fraction of cobalt in a Co3O4 lattice with another metal cation, known as doping, is a potential way to improve the performance of Co3O4 catalysts. The chemical bonding at the surface of Co3O4 could be modified by metal doping, which may in turn induce lattice imperfection and create oxygen vacancies that are beneficial to catalytic reaction. The effect of metal dopant features, including oxidation state, ionic radius, electronegativity, etc., on the physicochemical properties and redox ability of cobalt-based catalysts was extensively studied theoretically and practically [8–10].

Ni doping into a Co3O4 lattice enhanced propane oxidation reaction kinetics by promoting surface lattice oxygen activity and facilitating CO2 desorption [11]. The incorporation of Mn in Co3O4 increased surface Co2+ concentration and active oxygen, contributing to high activity in catalytic combustion of 1,2-dichlorobenzene (o-DCB) and retarding chlorination of o-DCB [12]. The doping of In2O3 induced the structural distortion of Co3O4 and promoted the catalytic performance of Co3O4 for CO oxidation [13]. Baidya et al. demonstrated that 15% Fe-doped Co3O4 can achieve superior catalytic activity and stability towards CO oxidation [14].

Although there have already been some reports on metal-doped Co3O4 catalysts that present desirable activity, the comparative study of different metal dopant effects on the catalytic activity of Co3O4 in different hydrocarbons oxidation is still limited and needs to be further explored. Recently, we have found that the precipitation agent could affect the catalytic activity of Co3O4. Among the investigated precipitation agent, sodium carbonate proved to be the most promising one. Considering this fact, in this study, the effect of metal-doping based on carbonate precipitation method on the physicochemical properties and redox ability of Co3O4 was investigated.

Herein, we prepared four metal-doped (Mn, Cu, Ni, and Fe) Co3O4 by a coprecipitation method. A comparative study of the catalytic behavior of pure and metal ion-substituted Co3O4 was investigated for the total oxidation of toluene and propane. A small amount of metal incorporated into the Co3O4 lattice affected the structure and redox property of Co3O4 and in turn led to different catalytic behavior as a function of the reactant used.

2. Results and Discussion

2.1. Chemical Composition, Structure, and Textural Properties

The chemical compositions of the as-prepared samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) measurement. The results are listed in Table 1. The cobalt mass ratio of pure cobalt oxide was 74.7 wt.%, close to the stoichiometric value of Co3O4 (73.4 wt.%). The substituted metal to cobalt molar ratios were similar to the theoretical one (5%), indicating the success of the coprecipitation process.
Table 1. Chemical composition, structural, and textural properties of the Co$_3$O$_4$ and M$_{0.05}$Co catalysts.

| Catalysts      | Co (wt.%) | M/Co (at.%) | D (nm) $^a$ | Strain (%) $^a$ | a (Å) $^a$ | SSA ($m^2$ g$^{-1}$) $^b$ | $V_{pore}$ (cm$^3$ g$^{-1}$) $^b$ |
|----------------|-----------|-------------|-------------|----------------|-----------|--------------------------|-------------------------------|
| Co$_3$O$_4$    | 74.7      | -           | 29.4        | 0.34           | 8.084     | 30                       | 0.08                          |
| Mn$_{0.05}$Co | 68.1      | 4.5         | 19.1        | 0.53           | 8.098     | 47                       | 0.19                          |
| Cu$_{0.05}$Co | 68.3      | 5.6         | 26.6        | 0.38           | 8.093     | 29                       | 0.07                          |
| Ni$_{0.05}$Co | 67.6      | 5.3         | 22.5        | 0.45           | 8.096     | 35                       | 0.11                          |
| Fe$_{0.05}$Co | 68.0      | 5.9         | 27.1        | 0.37           | 8.094     | 34                       | 0.09                          |

$^a$ Average crystalline size (D), strain, and lattice constant (a) obtained from XRD analysis. $^b$ Specific surface area (SSA) and total pore volume ($V_{pore}$) calculated from N$_2$ adsorption-desorption isotherm.

Powder X-ray diffraction (XRD) patterns of pure cobalt oxide and metal-doped cobalt oxides are shown in Figure 1. It is observed that all metal-doped cobalt oxides exhibited characteristic diffraction peaks corresponding to Co$_3$O$_4$ spinel structures (lattice constant $a = 8.0840$ Å, PDF # 74-2120) identical to pure cobalt oxide, no matter what kind of substituted metal was used, indicating that the doped metals were uniformly distributed in the samples, either in the lattice or on the surface. However, looking at the enlarged patterns for all M-Co$_3$O$_4$ samples, an evident shift of the most intense peak (311) to lower angles could be seen, suggesting an increase in the lattice constant due to metal substitution. The average crystalline sizes, strains, and the lattice constants of all samples were calculated and are listed in Table 1. Compared to pure Co$_3$O$_4$, all M-Co$_3$O$_4$ samples presented a smaller crystalline size, a bigger strain, and a larger lattice constant, especially for the Mn$_{0.05}$Co sample. This result demonstrates that some M ions were successfully introduced into the crystal lattice of Co$_3$O$_4$, leading to a lattice expansion of the spinel, thus generating a smaller crystalline size.

![Figure 1. (a,b) XRD patterns of the Co$_3$O$_4$ and M$_{0.05}$Co catalysts.](image)

Figure 2 shows the Fourier transform infrared (FTIR) spectra of Co$_3$O$_4$ and M$_{0.05}$Co samples. Two characteristic peaks at ca. 655 and 550 cm$^{-1}$ (with shoulders at higher frequencies), corresponding to vibrations of Co$^{3+}$ in tetrahedral sites and Co$^{2+}$ in octahedral sites in Co$_3$O$_4$ spinel structure respectively [15], were observed for all samples, in agreement of XRD analysis. However, some new peaks appeared in the case of Mn$_{0.05}$Co and Fe$_{0.05}$Co, which could be assigned to vibration modes of Mn–O and Fe–O, respectively [16,17]. In addition, the presence of Ni–O or Cu–O vibration modes could not be excluded since they were expected to be located in the same region of Co–O vibration modes and could be overlapped [18,19]. This phenomenon revealed that not all metal ions were successfully inserted into the matrix of Co$_3$O$_4$ lattice, some of them might form amorphous MO$_x$ species and distribute on the surface.
The N₂ adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distributions of undoped and doped Co₃O₄ samples are displayed in Figure 3. The type IV isotherm curves and H1-shaped hysteresis loops indicated the presence of slit-type mesopores originated from the accumulation of nanoparticles. The textural parameters of the different samples are summarized in Table 1. The specific surface areas (SSA) of all samples sit in the range of 30 to 47 m² g⁻¹. Among all samples, Mn₀.₀₅Co showed the largest SSA (47 m² g⁻¹) and biggest pore volume (0.19 cm³ g⁻¹), followed by the Ni₀.₀₅Co and Fe₀.₀₅Co samples. It should be noted that the average crystallite size of Cu₀.₀₅Co was smaller than that of pure Co₃O₄, while the SSA for Cu₀.₀₅Co was lower than that for pure Co₃O₄, indicating a strong agglomeration of the crystallites.

Raman spectra were recorded to investigate the effect of metal doping on the lattice distortion of the spinel. As shown in Figure 4, five characteristic bands at 665, 601, 507, 463, and 187 cm⁻¹ corresponding to stretching mode of spinel Co₃O₄ (A₁g, F₃̅g, F₂g, F₄g, and F₁̅g symmetry) were clearly observed for pure Co₃O₄ [5,20]. Compared to pure Co₃O₄, the Raman bands of the Mn₀.₀₅Co samples weakened and broadened because of the dissolution of M into the Co₃O₄ lattice, which induced lattice expansion and lattice distortion, as revealed by XRD analysis. The peak position and full width at half maxima (FWHM) of the most intense peak are listed in Table 2. Raman spectrum of Ni₀.₀₅Co...
underwent a red-shift, while that of Fe$_{0.05}$Co underwent a blue-shift. Ni$_{0.05}$Co exhibited the largest FMWH while Fe$_{0.05}$Co exhibited the smallest one.

![Figure 4. Raman spectra of the Co$_3$O$_4$ and Mn$_{0.05}$Co catalysts.](image)

### Table 2. Raman and temperature-programmed reduction in hydrogen (H$_2$-TPR) analysis of the Co$_3$O$_4$ and Mn$_{0.05}$Co catalysts.

| Catalysts | Raman Peak $^a$ (cm$^{-1}$) | FWHM $^a$ | Total H$_2$ Uptake (mmol g$^{-1}$) | H$_2$ Uptake Below 300 °C (mmol g$^{-1}$) |
|-----------|-----------------------------|-----------|-----------------------------------|------------------------------------------|
| Co$_3$O$_4$ | 667                         | 34        | 16.0                              | 3.0                                      |
| Mn$_{0.05}$Co | 672                         | 37        | 15.0                              | 2.5                                      |
| Cu$_{0.05}$Co | 667                         | 34        | 13.7                              | 8.1                                      |
| Ni$_{0.05}$Co | 660                         | 46        | 15.0                              | 3.2                                      |
| Fe$_{0.05}$Co | 684                         | 24        | 13.8                              | 2.1                                      |

$^a$ Peak position and FWHM of the most intense Raman peak.

#### 2.2. Reducibility

To investigate the effect of metal doping on the reducibility of Co$_3$O$_4$, H$_2$-TPR experiments were carried out; the results are shown in Figure 5, whereas the quantitative results of hydrogen consumption are summarized in Table 2. For pure Co$_3$O$_4$, the reduction initiated at 195 °C and finished at 400 °C. Two sequent peaks corresponding to the reduction of Co$^{3+}$→Co$^{2+}$ and Co$^{2+}$→Co$^0$ were clearly observed at 291 and 383 °C, respectively. However, after metal doping, the positions of these two peaks clearly changed. Moreover, some small peak shoulders that may arise from the reduction of doping species appeared (indicated by the arrows). In the case of Cu$_{0.05}$Co and Ni$_{0.05}$Co, both peaks shifted towards low temperature range, especially for Cu$_{0.05}$Co. The reduction of the Cu-doped sample started from 170 °C and ended at 360 °C, suggesting that the presence of Cu or Ni facilitated the Co$_3$O$_4$ reduction. Regarding Mn$_{0.05}$Co and Fe$_{0.05}$Co, the low-temperature peak appeared to be similar to that of the pure Co$_3$O$_4$, while the high-temperature peak moved to higher temperature zone, indicating that Mn or Fe doping could hinder the formation of metallic cobalt, which is beneficial for the redox circle during reaction between Co$^{3+}$ and Co$^{2+}$ [21]. The total hydrogen consumption amount decreased for all the metal-doped samples, suggesting the nonstoichiometric nature of the samples with metal doping. By comparing the hydrogen uptake below 300 °C, one can conclude that the low temperature reducibility ranks in the sequence Cu$_{0.05}$Co > Ni$_{0.05}$Co > Co$_3$O$_4$ > Mn$_{0.05}$Co > Fe$_{0.05}$Co. Based on the above reduction behaviors, Cu or Ni doping enhanced the reducibility of Co$_3$O$_4$, whereas Mn or Fe doping worsened it. This way, Cu$_{0.05}$Co was the most reducible sample.
Figure 5. H₂-TPR profiles of the Co₃O₄ and M₀.₀₅Co catalysts.

2.3. Catalytic Performance

2.3.1. Catalytic Activity and Stability in Toluene Oxidation

The catalytic performance of all the samples was evaluated in both toluene and propane oxidation. Regarding the toluene oxidation, three continuous heating–cooling loop tests were performed. Figure S1a presented the light-off curves of pure Co₃O₄ and metal-doped Co₃O₄ catalysts during the third continuous heating run. In the high conversion stage, toluene conversion to CO₂ exceeds 100% due to the accumulation of intermediates during the low conversion period [22]. Considering this fact, the light-off curves during the third continuous cooling run were used and are displayed in Figure 6, whereas the light-off temperatures at 10, 50, and 90% toluene conversion (T₁₀, T₅₀, and T₉₀) were listed in Table 3. The difference among the three catalytic cycles was imperceptible, demonstrating the excellent cycle stability of the Co₃O₄ and M₀.₀₅Co catalysts. All catalysts were able to achieve full conversion of toluene to CO₂ below 280 °C. After doping with Mn, Cu, or Ni, the catalytic performance of pure Co₃O₄ was obviously improved, being that the light-off curve shifted to lower temperature. However, the incorporation of Fe into Co₃O₄ resulted in a worse performance. Notably, the catalytic performance enhancement by metal doping is more pronounced in the low temperature stage than in the high one. In addition, the concentrations of CO produced during the toluene oxidation process over all catalysts were below 110 ppm (Figure S2a). Among them, Fe₀.₀₅Co with poor catalytic efficiency showed inferior selectivity. Nevertheless, the calculated carbon balances at 300 °C for all catalysts were higher than 95%, indicating the decent selectivity of the as-prepared cobalt-based catalysts.

Figure 6. Variation of the toluene conversion with the reaction temperature during the third consecutive cooling run over the Co₃O₄ and M₀.₀₅Co catalysts.
Table 3. Light-off temperatures at 10, 50, and 90% toluene conversion upon the cooling process.

| Catalysts      | 1st Run |         |         | 2nd Run |         |         | 3rd Run |         |         |
|----------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                | T_{10}  | T_{50}  | T_{90}  | T_{10}  | T_{50}  | T_{90}  | T_{10}  | T_{50}  | T_{90}  |
| Co_{3}O_{4}    | 223     | 235     | 256     | 223     | 235     | 256     | 223     | 235     | 256     |
| Mn_{0.05}Co    | 203     | 224     | 254     | 204     | 224     | 255     | 204     | 224     | 255     |
| Cu_{0.05}Co    | 211     | 228     | 251     | 211     | 228     | 251     | 211     | 228     | 251     |
| Ni_{0.05}Co    | 206     | 226     | 250     | 206     | 226     | 250     | 206     | 226     | 250     |
| Fe_{0.05}Co    | 234     | 244     | 270     | 234     | 244     | 270     | 234     | 245     | 270     |

In order to better compare the activity, the catalytic reaction rates of all catalysts at 210 °C were calculated and are listed in Table 4. This activity ranked as follows, Mn_{0.05}Co > Ni_{0.05}Co > Cu_{0.05}Co > Co_{3}O_{4} > Fe_{0.05}Co. Moreover, the activation energies (E_a) and pre-exponential factors (A) were estimated based on the slopes and intercepts of the Arrhenius plots (Figure S3a). Diverse values of the activation energy ranging from 142 kJ mol^{-1} to 231 kJ mol^{-1} were obtained. The activation energies and pre-exponential factors here showed did not correlated with the activity, which can be explained by the compensation effect (Figure S4) [23,24].

Table 4. Reaction rates (r) at 210 °C, apparent pre-exponential factors (A), apparent activation energies (E_a), and coefficient of determination (R^2) for toluene oxidation over various catalysts (reaction conditions: toluene concentration = 1000 ppm, O_2 concentration = 21 vol.%, and WHSV = 40,000 mL h^{-1} g^{-1}).

| Catalysts | r (10^{-9} mol g_{Co}^{-1} s^{-1}) | InA     | E_a (kJ mol^{-1}) | R^2  |
|-----------|---------------------------------|---------|------------------|------|
| Co_{3}O_{4}| 1.5                             | 30.5 ± 0.8 | 196 ± 3         | 0.995|
| Mn_{0.05}Co| 14.6                            | 18.7 ± 0.5 | 142 ± 2         | 0.998|
| Cu_{0.05}Co| 6.4                             | 40.6 ± 1.2 | 231 ± 5         | 0.997|
| Ni_{0.05}Co| 10.2                            | 24.3 ± 1.2 | 165 ± 5         | 0.993|
| Fe_{0.05}Co| 0.5                             | 35.8 ± 0.9 | 222 ± 4         | 0.997|

The long-term stability of the catalysts was assessed at 20–25% of toluene conversion after the first cooling run. As shown in Figure 7, the conversion declined for all catalysts to some extent after 5 h, remaining invariable throughout the test. The Mn_{0.05}Co, Cu_{0.05}Co, and Ni_{0.05}Co catalysts exhibited similar stability, with ~15% decrease in toluene conversion during the whole process. The Co_{3}O_{4} and Fe_{0.05}Co catalysts deactivated more severely, ~20% of toluene conversion drop was observed. In order to figure out the reason causing catalyst deactivation, a post-calcination treatment in air flow was carried out after 24 h stability test; the CO_2 evolution as a function of time on stream was plotted in Figure S5. The maximum in the CO_2 concentration could arise from the catalytic oxidation of adsorbed toluene or intermediate into CO_2 [25]. The time for reaching this maximum CO_2 concentration was dependent on the catalytic activity of the different catalysts and likely on the reaction temperatures (varied from 215 to 240 °C). The higher the reaction temperature, the faster the CO_2 desorption on the catalyst surface. The area of this peak reflected the amount of toluene/intermediate adsorbed in the catalyst. Among these catalysts, Fe_{0.05}Co exhibited the largest peak area, suggesting its excellent CO_2 adsorption capacity. To verify the reversibility of this deactivation for catalyst Co_{3}O_{4}, a stability test was conducted after the calcination treatment (Figure S6). Identical stability curve was observed after the calcination step, demonstrating that it is possible to completely regenerate the catalyst.
2.3.2. Catalytic Activity and Water Resistance in Propane Oxidation

On the other hand, the light-off curves of the propane oxidation for pure Co$_3$O$_4$ and metal-doped Co$_3$O$_4$ catalysts during the cooling run are displayed in Figure 8. Table 5 summarized the temperatures at which 10, 50, and 90% of propane conversion was reached. Propane can be converted into CO$_2$ below 280 °C for all of the catalysts. However, totally different trends in the catalytic performance of propane and toluene oxidation were observed. For propane oxidation, pristine Co$_3$O$_4$ was the most active catalyst. The doping with Cu, Ni, or Fe was detrimental for the catalytic performance of pure Co$_3$O$_4$, being that the light-off curve shifted to higher temperature. This detrimental phenomenon was especially remarkable over Cu$_{0.05}$Co. Fortunately, the catalytic performance remained practically unaltered after the incorporation of Mn. The concentrations of CO and propene produced during the propane oxidation process over all catalysts were 0 ppm (no shown) and <5 ppm (Figure S2b), respectively, suggesting the excellent selectivity of the catalysts, which was further confirmed by the good carbon balance throughout the catalytic system (>99%).

![Figure 7. Toluene oxidation test conducted at 20–25% of toluene conversion during 24 h.](image)

![Figure 8. Variation of the propane conversion with the reaction temperature during the cooling run over the Co$_3$O$_4$ and M$_{0.05}$Co catalysts.](image)
Table 5. Light-off temperatures at 10, 50, and 90% propane conversion upon cooling process in normal condition or in the presence of 4.4 vol.% water.

| Catalysts  | Normal Condition | In 4.4 vol.% Water |
|------------|------------------|---------------------|
|            | T10 | T50 | T90 | T10 | T50 | T90 |
| Co3O4      | 161 | 199 | 226 | 185 | 218 | 245 |
| Mn0.05Co   | 162 | 201 | 227 | 178 | 215 | 245 |
| Cu0.05Co   | 180 | 225 | 257 | 206 | 248 | 287 |
| Ni0.05Co   | 170 | 213 | 245 | 199 | 243 | 290 |
| Fe0.05Co   | 169 | 210 | 241 | 184 | 219 | 255 |

Likewise, the catalytic reaction rates of all catalysts in the propane oxidation at 160 °C were calculated and are listed in Table 6. They followed the order, Co3O4 ≈ Mn0.05Co > Fe0.05Co ≈ Ni0.05Co > Cu0.05Co. In addition, from Arrhenius plots (Figure S3b), various Ea (67–79 kJ mol⁻¹) were obtained (Table 6). Compensation effect appeared again (Figure S4) [23,24], namely, the higher the value of Ea, the higher the value of lnA.

Table 6. Reaction rates (r) at 160 °C, apparent pre-exponential factors (A), apparent activation energies (Ea), and coefficient of determination (R²) for propane oxidation over various catalysts (reaction conditions: propane concentration = 1000 ppm, O2 concentration = 21 vol.% and WHSV = 40,000 mL h⁻¹ g⁻¹).

| Catalysts  | r (10⁻⁸ mol gCat⁻¹ s⁻¹) | lnA | Ea (kJ mol⁻¹) | R²   |
|------------|------------------------|-----|---------------|------|
| Co3O4      | 6.1                    | 4.2 ± 0.2 | 76.2 ± 0.8 | 0.999 |
| Mn0.05Co   | 6.1                    | 3.0 ± 0.3 | 72.0 ± 0.9 | 0.999 |
| Cu0.05Co   | 3.0                    | 0.8 ± 0.1 | 66.8 ± 0.4 | 0.999 |
| Ni0.05Co   | 4.2                    | 2.3 ± 0.2 | 70.9 ± 0.7 | 1.000 |
| Fe0.05Co   | 4.2                    | 4.5 ± 0.2 | 78.6 ± 0.7 | 0.999 |

As in every oxidation process, water is inevitably present either as a part of the inlet stream or as a combustion product, which would alter reaction equilibrium and in turn cause deactivation, due to either the competitive adsorption between H2O and reactant molecules or the formation of inert hydroxyls groups on the catalyst surface [26]. Therefore, the effect of presence of H2O on the catalytic oxidation of propane was investigated. As shown in Figure 9, a decrease in propane conversion was observed for all studied catalysts when 4.4 vol.% of H2O was present in the reactant gas. Their T50 values were 9–30 °C higher than those obtained in the dry reaction condition. Among these catalysts, Fe0.05Co presented the best water tolerance for propane oxidation since it maintained good activity to a certain extent. Ni0.05Co was the most sensitive sample to H2O. On the other hand, Mn0.05Co still showed desirable catalytic performance, with T10 as low as 178 °C.

Figure 9. Variation of the propane conversion with the reaction temperature during the cooling run over the Co3O4 and Mn0.05Co catalysts in the absence and presence of 4.4 vol.% water.
2.4. Discussion

By metal doping, smaller crystalline sizes and larger specific surface areas were obtained for the Mn$_{0.05}$Co catalyst. XRD and Raman analysis demonstrated that other metal (Mn, Cu, Ni, or Fe) was inserted into the structure of Co$_3$O$_4$. This was corroborated by lattice expansion and broadening of Raman bands. Furthermore, FTIR spectra revealed that there were some metal oxides (Mn, Fe) distributed on the surface of Co$_3$O$_4$. H$_2$-TPR results confirmed the strong interaction between M and Co in the Mn$_{0.05}$Co catalyst, as the reduction behavior changed much after M-doping.

The effect of the metal doping on the catalytic performance of all the catalysts in the toluene and propane oxidation reactions was not always the same. A catalyst that was active for toluene oxidation may not be good for propane oxidation. That was the case, for example, for catalyst Cu$_{0.05}$Co. This may be due to the different nature of these two reactant molecules (type of C–C bonds and molecular sizes) and the different reaction mechanisms involved for these two reactions [27]. It is generally accepted that the total oxidation of toluene over Co-based catalysts proceeds through a Mars–van Krevelen mechanism: toluene first reacts with the mobile lattice oxygen species to produce CO$_2$ and H$_2$O accompanied by the reduction of Co$^{3+}$ to Co$^{2+}$, meanwhile O$_2$ molecules in air replenish the reduced catalyst and complete the redox cycle $\text{Co}^{3+} \rightleftharpoons \text{Co}^{2+}$ [28,29]. The promoted catalytic performance of Cu$_{0.05}$Co and Ni$_{0.05}$Co for toluene oxidation could be attributed to the strong synergistic effect between cobalt and doped metal cations. Lattice oxygen could be much more easily abstracted by hydrogen from Cu$_{0.05}$Co and Ni$_{0.05}$Co than from Co$_3$O$_4$, increasing the mobility of lattice oxygen and resulting in better oxidation ability. For propane oxidation, the amount of surface adsorbed oxygen is reported to be the determining factor [30,31]. Thus, metal doping may influence the chemical status of surface/chemisorbed oxygen in M$_{0.05}$Co, thus leading to a different catalytic behavior in propane oxidation.

Anyhow, benefitting from its big strain and large surface area, Mn$_{0.05}$Co is the best catalyst prepared in this study. It is efficient for both toluene and propane oxidation reactions. Hopefully, it could be considered as a potential industrial catalyst for removing hydrocarbon pollutants by oxidation processes.

3. Experimental

3.1. Catalyst Preparation

Cobalt oxide and M-doped (Mn, Fe, Ni, and Cu) cobalt oxide catalysts were prepared by a coprecipitation method using sodium carbonate as the precipitant. All chemicals were obtained from Sigma-Aldrich and used as received. Twenty millimoles of Co(NO$_3$)$_2$·6H$_2$O and 1 mmol of second metal salt (Mn(Ac)$_2$·4H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, or Fe(NO$_3$)$_3$·9H$_2$O) were dissolved in 100 mL of distilled water. Twenty-two millimoles of Na$_2$CO$_3$ was dissolved in 100 mL of distilled water. The resulting Na$_2$CO$_3$ aqueous solution was added to the metal salts aqueous solution. After being stirred at room temperature for 1 h, the solid was separated and fully washed by centrifugation and redispersion. The obtained wet cake was dried at 80 °C overnight and then calcined in a muffle furnace at 200 °C for 1 h and at 500 °C for 1 h with a temperature ramp rate of 2 °C/min$^{-1}$. The final products were referred to as M$_{0.05}$Co, where M is the doped metal and 0.02 is the atomic ratio of M:Co.

3.2. Catalyst Characterization

The chemical composition of the samples was measured by ICP-OES (Horiba Jobin Yvon, Paris, France). Prior to the determination, the metal oxides were dissolved in a mixture of inorganic acids (H$_2$SO$_4$ and HNO$_3$).

FTIR spectra were recorded using a FT-IR C92712 spectrometer (PerkinElmer, Waltham, MA, USA) in attenuated total reflectance mode at an instrument resolution of 1 cm$^{-1}$ over a range of 400 to 4000 cm$^{-1}$. 
Nitrogen adsorption−desorption isotherms were obtained using a TRISTAR II apparatus (Micromeritics, Norcross, GA, USA) at −196 °C. Before analysis, each sample was pretreated at 300 °C for 3 h under primary vacuum. The specific surface areas of the samples were determined by the standard Brunauer–Emmett–Teller (BET) procedure. The total pore volume and the pore size distribution were calculated using the BJH method.

Powder X-ray diffraction (XRD) patterns were recorded on a D5005 diffractometer (Bruker, Karlsruhe, Germany) equipped with a Cu Kα radiation (λ = 0.154184 nm) and a graphite monochromator on the diffracted beam. Samples were scanned from 10° < 2θ < 80° with a step size of 0.02° and a counting time of 2 s per step.

Raman spectra were recorded by a LabRam HR spectrometer (Horiba, Paris, France) using Ar+ laser beam of 514 nm wavelength for an excitation.

Temperature-programmed reduction experiments in hydrogen (H₂−TPR) were performed on a commercial Micromeritics AutoChem 2950 HP (Micromeritics, Norcross, GA, USA) unit with TCD detection. In each test, 0.05 g of sample was pretreated under 50 mL/min of Ar flow at 350 °C for 0.5 h. After cooling down to 45 °C, reduction was performed under 50 mL/min of 5 vol.% H₂/Ar from 45 to 800 °C at a rate of 10 °C/min. A trap cooled with isopropyl alcohol/liquid nitrogen slurry (−80 °C) was applied to remove water that could distort the TCD signal.

3.3. Catalytic Activity Tests

For each test, 150 mg of catalyst mixed with ~600 mg of silicon carbide was packed inside a U-shaped reactor (220 mm in length and 4 mm in internal diameter) with a bed height of 6 mm.

For the toluene oxidation tests, the reactant gas mixture, composed of 1000 ppm toluene and synthetic air (21 vol.% O₂ + 79 vol.% N₂), with a total flow of 100 mL/min, was fed into the reactor before being heated from room temperature to 150 °C (5 °C/min) and held at this temperature for 0.5 h to stabilize the system. Then, a second temperature ramp of 2 °C/min was run until 350 °C and held at this temperature for 1 h. Next, the reactor was cooled down to 150 °C (2 °C/min). Three consecutive heating–cooling catalytic cycles were performed to evaluate the catalytic stability. The concentrations of CO and CO₂ were in situ recorded by a Rosemount Xtreme Gas Infrared Analyzer (Emerson Electric Co., St. Louis, MO, USA). The toluene conversion was calculated as follows,

\[ X_{C_7H_8}(\%) = \frac{[CO_2]}{7[C_7H_8]} \times 100 \]  

where [CO₂] and [C₇H₈] represent the outlet CO₂ concentration and the initial toluene concentration, respectively.

Regarding the propane oxidation, after 100 mL/min of the reactant gas mixture (0.1 vol.% propane + 21 vol.% O₂ + 79 vol.% He) was introduced into the reactor at room temperature, the reactor was heated from room temperature to 100 °C (5 °C/min) and held at this temperature for 0.5 h to stabilize the system. Subsequently, the temperature was increased from 100 °C to 350 °C (2 °C/min) and held at this temperature for 1 h. Next, the reactor was cooled down to 100 °C (2 °C/min). Gas effluents were analyzed by an online micro gas chromatograph (SRA % GC-R3000) coupled with a thermal conductivity detector. The propane conversion was calculated as follows,

\[ X_{C_3H_8}(\%) = \frac{[CO_2]}{3[C_3H_8]} \times 100 \]  

where [CO₂] and [C₃H₈] are the outlet CO₂ concentration and the initial propane concentration, respectively.

4. Conclusions

Cobalt oxides doped with Mn, Cu, Ni, or Fe were successfully synthesized via simple carbonate coprecipitation method. XRD and Raman analysis proved the formation of the cubic spinel phase
CoO\textsubscript{4} after the incorporation of dopants. The Mn\textsubscript{0.05}Co sample exhibited the smallest crystalline size and biggest strain. The MnO\textsubscript{x} and FeO\textsubscript{x} phases could be detected on the surface of Mn\textsubscript{0.05}Co and Fe\textsubscript{0.05}Co by FTIR spectra. The H\textsubscript{2}–TPR study demonstrated the strong interaction between doped metal and cobalt. Cu\textsubscript{0.05}Co appeared to be the most reducible sample. The catalytic activities were investigated for the total oxidation of toluene and propane. Mn\textsubscript{0.05}Co exhibited undoubtedly the highest catalytic activity in both reactions. However, the activity for toluene and propane oxidation for the other catalysts was different. Cu\textsubscript{0.05}Co and Ni\textsubscript{0.05}Co were more active in toluene oxidation than pure CoO\textsubscript{4}, whereas the opposite occurred for propane oxidation. Although the doping of Fe lowered the activity of pure CoO\textsubscript{4} in both cases, it allowed for the acquisition of better water-resisting catalysts for propane oxidation. Different mechanisms and different rate-determining factors are supposed to explain this activity variation as a function of the molecules to be oxidized.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/8/865/s1, Figure S1: Variation of the (a) toluene conversion (b) propane conversion with the reaction temperature during the heating run, Figure S2: Evolution of (a) CO concentration in toluene oxidation and (b) C\textsubscript{3}H\textsubscript{6} concentration in propane oxidation during one heating–cooling catalytic cycle over the CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts, Figure S3: Arrhenius plots for (a) toluene oxidation (b) propane oxidation over CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts. (reaction conditions: toluene/propene concentration = 1000 ppm, O\textsubscript{2} concentration = 21 vol.\% and WHSV = 40,000 mL h\textsuperscript{-1} g\textsuperscript{-1}). Figure S4: Constable plot of apparent pre-exponential factors as a function of apparent activation energies for toluene and propane oxidation over CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts, Figure S5: CO\textsubscript{2} evolution as a function of time on stream in air flow after 24-h stability test, Figure S6: Toluene conversion to CO\textsubscript{2} as a function of time on stream over CoO\textsubscript{4} catalyst at 230 °C.

**Author Contributions:** This study was done jointly by all authors. W.Z. prepared the catalysts, performed the heating and cooling catalytic cycle over the CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts, Figure S3: Arrhenius plots for (a) toluene oxidation (b) propane oxidation over CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts. (reaction conditions: toluene/propene concentration = 1000 ppm, O\textsubscript{2} concentration = 21 vol.\% and WHSV = 40,000 mL h\textsuperscript{-1} g\textsuperscript{-1}), Figure S4: Constable plot of apparent pre-exponential factors as a function of apparent activation energies for toluene and propane oxidation over CoO\textsubscript{4} and Mn\textsubscript{0.05}Co catalysts, Figure S5: CO\textsubscript{2} evolution as a function of time on stream in air flow after 24-h stability test, Figure S6: Toluene conversion to CO\textsubscript{2} as a function of time on stream over CoO\textsubscript{4} catalyst at 230 °C.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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