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# Effect of alkali and alkaline earth metal dopants on catalytic activity of mesoporous cobalt oxide evaluated using a model reaction

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#### **Graphical Abstract**

#### Highlights

- 1. Synthesis of  $Co_3O_4$  and doped- $Co_3O_4$  catalysts is described.
- 2. The  $Co_3O_4$  catalysts are active in oxidation of morin.
- 3. The H<sub>2</sub>-TPR and XPS analyses confirm electron structure change.

#### Abstract

Herein we report the synthesis of mesoporous cobalt oxides in pure (Co<sub>3</sub>O<sub>4</sub>) and alkali and alkaline earth metal doped form (Li-, Ca-, Cs-, and Na-, K-, and Mg/Co<sub>3</sub>O<sub>4</sub>) via the inverse micelle method. The as-prepared materials were characterized by powder X-ray diffraction (pXRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), nitrogen sorption (BET), hydrogen-temperature-programmed reduction (H<sub>2</sub>-TPR), and X-ray photoelectron spectroscopy (XPS). Characterization results suggested that the as-synthesized materials are of amorphous and mesoporous nature. Their catalytic activity was investigated using a model reaction, namely the liquid-phase morin oxidation. Results revealed pure cobalt oxide to be the better catalyst compared to its doped counterparts. The stability of Li/Co<sub>3</sub>O<sub>4</sub> material was investigated exemplarily by recycling and reusing the catalysts for as many as four catalytic cycles. Conversion of morin was complete in all runs and no significant metal leaching could be detected by the use of inductively coupled plasma mass spectrometry (ICP-MS).

**Keywords:** Morin oxidation; reducible metal oxides; metal dopants, effective kinetics, transport limitation.

#### Introduction

Model reactions have been successfully applied to study catalytic systems [1-4]. Over the past decades several reports emerged describing kinetics of model reactions such as e.g. morin oxidation and 4-nitrophenol reduction [5-7]. Most of these studies employed metallic nanoparticles as catalysts [8] and results suggested that these model reactions take place on the

surface of the catalyst [9, 10]. Not surprisingly, surface properties such as surface area and electronic structure of the catalyst are of significant importance in heterogeneous catalysis [11]. Previous studies have indicated that an increase in the surface area of the catalyst results in increased activity, and changes in the electronic structure of the catalyst impact the activity either in a positive or negative way [12]. Such changes of the catalytic system can be induced in several ways, including, but not limiting to the immobilization of catalytically active species [13, 14], reduction or oxidation of the catalyst [15], or the use of doping agents [16-18]. In catalytic oxidation with oxygen-rich catalysts such as reducible transition metal oxides, it is believed that the lattice oxygen participates in the oxidation process according to a Mars van Krevelen mechanism [19, 20]. Thus, the extent of catalyst reduction or oxidation is of significant importance.

Metal oxides have been successfully employed as catalysts in a wide range of oxidation reactions and the electronic structure is believed to be one of the defining properties of these oxide catalysts. Doped metal oxide catalysts are reported to be better catalysts in many oxidation reactions. Studies on NiO system doped with Zr proved the positive effect of doping with Zr in oxidative dehydrogenation of ethane at high temperatures [21]. In this case, the improved selectivity indicate a change in chemical environment around the active Ni centers. Such a change in chemical environment of the active metal can be brought about by changes in acidity and basicity of the transition metal and the lattice oxygen, respectively. This then lead to altered strength of chemisorption of the substrate and intermediates, and the rate of product desorption. Depending on the electronic properties of the valence band of the dopant, it can either bind strongly or weakly to the lattice oxygen, thus, the Lewis acidity of the metal cation changes. Other materials with tuneable properties were reported e.g. by Tian et al. [22]. These materials have mixed phases of manganese oxides in the lattices such as Mn<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub>. With these materials, catalytic conversions of 8 and 10% were achieved for the oxidation of cyclohexane and *n*-hexane, respectively. Recently, ternary oxides of Mn and Co were reported to have different catalytic activities due to different interactions with Ru which was used as the third metal [23].

Based on these observations, were became interested in the effects of different alkali and alkaline earth metal doping agents on mesoporous cobalt oxide in oxidation reactions. Morin oxidation

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was chosen by virtue of being a model reaction and because of the ease at which the reaction can be monitored using fast and reliable spectroscopic techniques such as UV-Visible spectrophotometry. Scheme 1 shows the oxidation of morin to morin oxide and its overoxidation to multiple phenolic acids.



Scheme 1. Oxidation of morin to morin oxide and overoxidation to multiple products.

In the past, information gained from morin oxidation has been used to elucidate the mechanism of oxidation of similar flavonoids such as e.g. quercetin. It was reported that the presence of  $H_2O_2$  as an oxidant is essential for generation of characteristic fragments and the positions of the hydroxyl groups determine the types of products formed [24]. Later, it was then suggested that biomimetic chemical oxidations of naturally occurring polyphenols may help elucidate oxidation mechanisms in e.g. food commodities [25].

#### **Experimental**

#### Materials and chemicals

The cobalt(II) nitrate hexahydrate (99 %), morin monohydrate ( $\geq$ 99 %), poly(ethylene glycol)block-poly(propylene glycol)-block-poly(ethylene glycol) (P-123), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30 % in water), 1-butanol ( $\leq$ 99 %)were all purchased from Sigma-Aldrich and used without further purification. Nitrate salts of cesium (99 %), magnesium ( $\leq$ 99 %), sodium, and lithium nitrate (Reagent Plus) were also purchased from Sigma-Aldrich and used without further purification. Anhydrous sodium carbonate (99 %), sodium hydrogen carbonate (99.5 %), calcium nitrate ( $\geq$ 98 %) and potassium nitrate (99 %) salts were purchased from Associated Chemical Enterprises. Milli-Q water (18 M $\Omega$ ·cm) was used in all experiments.

#### Catalyst synthesis

The preparation of the catalysts was achieved with the use of a soft-template approach. In a typical experiment, 8 g of templating polymer P-123 was dissolved in 60 ml of 1-butanol. A 20 g of the metal precursor, cobalt(II) nitrate hexahydrate, was added and allowed to dissolve. At this stage, the dopants were added and allowed to react for 20 minutes under vigorous stirring. Then, 10.3 ml of 55 % nitric acid was added and the mixture was allowed to react for 3 hours. The resulting pink gel was placed in an oven set at 60 °C for 12 hours to evaporate the solvent. Then, a heating cycle followed. The material was placed in an oven at 120 °C for 5 hours. The powder obtained was washed with ethanol and centrifuged and dried in a vacuum oven for 12 hours. The dried powder was further calcined at 150 °C for 12 hours.

#### Catalyst characterization

Prior to catalytic evaluation, the catalysts were characterized using different physical techniques. For the pXRD analysis, the materials were carefully ground and analyzed with a Rigaku MiniFlex 600 powder diffractometer equipped with Cu K $\alpha$ 1 ( $\lambda$  = 0.1542 nm) radiation source. Low angle measurements were performed between 0.5 and 10° 20 at a step rate of 0.1 °/min and high angle measurements were performed between 10 and 90° 20 with a step rate of 0.4 °/min. The resulting p-XRD pattern was matched using the Match! 2 software [26].

BET measurements were performed using a Micromeritics ASAP 2460 surface area and porosity analyzer. Prior to the analysis, the samples were degassed with  $N_2$  gas at 90 °C for 12 hours. All the measurements were carried out at -196 °C and the pore volume and pore sizes were calculated from the adsorption curves using the BJH model.

The TEM and HRTEM analyses were performed using a JEOL-JAM 2100F electron microscope operating at 200 kV. The catalytic materials were dispersed in small amounts of ethanol and sonicated for 30 minutes. Thereafter, they were placed on top of carbon-coated Cu-grids.

The SEM analysis was performed on a Tescan Vega 3LMH scanning electron microscope with the samples carbon-coated on copper grids using an Agar Turbo Carbon Coater.

The amount of dopants in the catalysts was determined by Spectro Acros inductively coupled plasma omission electron spectroscopy (ICP-OES). The materials were digested using aqua regia

(1:3 v/v nitric acid and hydrochloric acid). Catalyst leaching test was done on a Shimadzu ICPMS-2030 spectrometer.

The H<sub>2</sub>-TPR measurements were carried out using an AutoChemII from Micromeritics. The analysis was performed between 25 and 900 °C with 10:90 H<sub>2</sub>-He ratio at a temperature ramping rate of 10 °C/minute. Furthermore, CO<sub>2</sub>-TPD analyses was carried out using the same instrument. A mixture with a ratio of 10:90 carbon dioxide and helium was used as a probe gas. Analysis was carried out with a ramping rate of 3 °C/min in the temperature range of 30 to 550 °C.

XPS data were acquired at room temperature with a SPECS Phoibos 150 electron energy analyser, using a monochromatised Al K $\alpha$  photon source (hv = 1486.71 eV). The overall energy resolution was set to 0.5 eV for all the spectra. The binding energy was calibrated with respect to the main peak in the C 1*s* core level (284.6 eV). To counteract the effect of surface charging, samples were irradiated with a low energy electron flood gun during measurements (electron energy: 3 eV, emission current: 20 mA).

#### Catalytic evaluation

All catalytic runs were performed in the dark in a 50 ml round-bottom flask covered with silver foil. Briefly, a  $25 \times 10^{-3}$  M morin stock solution was prepared in  $5 \times 10^{-3}$  M carbonate buffer. In a typical reaction,  $1 \times 10^{-3}$  M of morin and  $10 \times 10^{-3}$  M of H<sub>2</sub>O<sub>2</sub> were used. The catalyst concentration was varied between  $3.46 \times 10^{-6}$  M and  $34.7 \times 10^{-6}$  M. Prior to the catalytic reaction, the solid catalysts were dispersed in de-ionized water (0.05 g in 10 ml de-ionized water). Sampling was performed at three minutes intervals. Monitoring of the catalytic reaction progress was performed using a Shimadzu UV-1800 UV-Vis spectrophotometer at  $\lambda$  410 nm.

Catalysts stability was investigated by recycling the catalysts and reusing it for as many as four cycles. The fine  $\text{Li}/\text{Co}_3\text{O}_4$  catalyst powder was filtered over a 5 µm frit and the supernatant was analyzed for Li and Co ions using Shimadzu ICPMS-2030 to investigate leaching of the material during the reaction.

#### Results

#### Catalyst characterization

The powder X-ray diffraction patterns obtained in low angle measurements for the pure and doped-cobalt oxides (Figure 1(a)) indicate that the materials have long-range mesoporous structures. This is evidenced by the fact that diffraction took place below 2° 20 range. The high angle measurements shown in Figure 1(b) confirm a spinel structure of the synthesized cobalt oxide (JCPDS 090418). Furthermore, the crystallite system was found to be cubic by Match !2 software. Usually in low angle measurements by conventional diffractometer set-ups, similar features are observed. The low angle features observed herein are characteristic of the assynthesized materials as there is a clear distinction between them and a non-porous cobalt oxide standard, Figure S1 in the ESI.



**Figure 1:** Diffraction pattern of pure and doped cobalt oxides. Graphs in (a) show low angle diffraction between  $0.5^{\circ}$  and  $2^{\circ} 2\theta$  range and in (b) is the wide angle diffraction patterns

measured between  $20^{\circ}$  and  $65^{\circ} 2\theta$ . The N<sub>2</sub> sorption results showing (c) type IV hysteresis loops and (d) the pore size distribution of pure and doped cobalt oxides.

Figure 1(c-d) shows the type IV hysteresis loops and pore size distributions. The surface properties such as the surface area, pore volume, and pore size were determined through nitrogen sorption experiments. All the synthesized catalysts appeared to be mesoporous in nature and type IV hysterisis loops, which suggest the mesoporous nature, were obtained from adsorption and desorption branches. The pure cobalt oxide has the largest surface area compared to all the doped catalysts. It is important to note that the average pore diameter of cobalt oxide increased upon doping, thus, leaving the pure cobalt oxide with the highest pore volume compared to all other catalysts. Table 1 show the surface properties of the synthesized pure and doped cobalt oxide.

Catalyst	$S_{BET}^{a}$	$V_{pore}{}^b$	$D_{pore^{c}}$	Crystallite size <sup>d</sup>	% doping <sup>e</sup>	Basicity
	(m <sup>2</sup> /g)	$(cm^{3}/g)$	(nm)	(nm)		(µg CO <sub>2</sub> )
Co <sub>3</sub> O <sub>4</sub>	32.9	0.93	12	22	-	56.1
Li/Co <sub>3</sub> O <sub>4</sub>	10.7	0.04	15	48	2.4	14.5
Na/Co <sub>3</sub> O <sub>4</sub>	17.3	0.05	13	86	2.1	75.7
K/Co <sub>3</sub> O <sub>4</sub>	4.7	0.03	18	15	2.3	-
Cs/Co <sub>3</sub> O <sub>4</sub>	17.0	0.06	13	36	2.4	145.1
Mg/Co <sub>3</sub> O <sub>4</sub>	22.1	0.08	15	40	2.6	224.3
Ca/Co <sub>3</sub> O <sub>4</sub>	20.8	0.11	19	32	2.4	441.5

 Table 1: Surface properties of pure and doped cobalt oxide obtained from N2 sorption experiments.

<sup>*a*</sup> BET surface area, <sup>*b*</sup> pore volume calculated from desorption branch (BJH model), <sup>*c*</sup> pore diameter calculated from the desorption branch (BJH model), and <sup>*d*</sup> Crystallite sizes calculated using Scherrer equation. <sup>*e*</sup> dopants %loading as determined by ICP-OES.

TEM images revealed the porous nature of the synthesized cobalt oxide particles and the morphology of the cobalt oxide particles did not change after doping. A wide range of shapes were observed for both the pure and doped cobalt oxide particles. From the scanning electron microscope images, the distribution of size varied from mostly larger to smaller particles. Figure

2 shows TEM and SEM micrographs of pure and Li/Co<sub>3</sub>O<sub>4</sub> (also see Figure S2 and S3 in ESI for the remaining materials).



**Figure 2:** TEM images of (a) pure cobalt oxide and (b) lithium doped cobalt oxide showing mesoporous nature. SEM images for (c) pure cobalt oxide and (d) lithium-doped cobalt oxide showing the morphology of the catalysts.

In oxidation reactions it is important to investigate reducibility of the catalysts as it relates to different catalytic activities [18]. The H<sub>2</sub>-TPR revealed the temperatures at which the catalysts can be reduced. Based on the results obtained, the catalysts were reduced at fairly low temperatures compared to other catalysts such as Ni-Zr-O catalysts [21]. The reduction peaks of pure mesoporous oxide shifted slightly upon doping with alkali and alkaline earth metals. Although cesium and lithium did not affect the reduction temperature of pure cobalt oxide significantly, there were significant shifts to higher temperatures for most dopants. This shifting

to higher temperatures of reduction peaks upon doping is consistent with literature reports [27]. Figure 3a illustrates graphically the temperature-programmed reduction results.



**Figure 3:** (a) H<sub>2</sub>-TPR for pure and doped-Co<sub>3</sub>O<sub>4</sub> catalysts and (b) the O 1s core level electrons XPS spectrum for undoped and doped Co<sub>3</sub>O<sub>4</sub> catalysts.

In Figure 3b, XPS data of the O 1s core level electrons show three components. Component 1 is the one on the higher binding energy side of the main peak, and it is due to oxygen vacancies in the main  $Co_3O_4$  matrix, component 2 (or the main peak) originates from stoichiometric oxygen in  $Co_3O_4$ , and component 3 only appears in the doped catalysts, and can be attributed to charge transfer from the dopant to the oxygen ions.

For the transition metal component, Co changes in the chemical environments of the Co  $2p_{1/2}$  and Co  $2p_{3/2}$  peaks upon doping were observed. A slight shift towards lower binding energies is observed upon doping, Figure 4 and Figure S4 in ESI. However, XPS analysis did not pick up all

the dopants. Most notable, is the absence of the Li peak. This is due to the low % loading and due to Li being a light element. The peaks for other dopants are shown in Figure S5 and the survey spectra is shown in Figure S6 in ESI. The influence of doping on the binding energy is evident in all doped catalysts. The line shape of the core level is composed of two sets of peaks corresponding to  $2p_{3/2}$  and  $2p_{1/2}$  spin-orbit states, whose centroids are located at binding energies of ~779 and ~794 eV, respectively, separated by a spin-orbit splitting of 15.1 eV. The Co  $2p_{3/2}$  binding energy region is located between 773 eV and 791 eV, while the Co  $2p_{1/2}$  binding energy region is located between 791 eV. The Co 2p line shape of the undoped catalyst can be fitted with three spin-orbit doublets, corresponding to  $Co^{2+}$  and  $Co^{3+}$  states. The dashed spin-orbit doublet, Figure 4 (bottom), which is not present in the undoped catalyst, consistently appears in the Co 2p core level spectra of all doped catalysts. It is located at about +1.8 eV relative to the main Co<sup>2+</sup> component. It can attributed to charge transfer from the dopant to cobalt. It is either an additional oxidation state for Co (i.e. Co<sup>1+</sup> in this case), or a "shifted" Co<sup>2+</sup> state due to the charge transfer mentioned above.



**Figure 4:** Changes in binding energy for pure and doped metal oxides determined by XPS analysis. (a) Pure Co<sub>3</sub>O<sub>4</sub> and (b) Cs/Co<sub>3</sub>O<sub>4</sub>.

From the CO<sub>2</sub>-TPD experiments, the dopants increased the basic sites of the catalysts. One interesting observation is that the basic sites increase with increase in the valence of the alkali metal. The same trend is observed for alkaline earth metals. Furthermore, alkaline earth metals appeared to increase the total basicity of the catalyst more than the alkali counterparts. The TPD plots can be seen in Figure S7 in the supplementary information.

#### Catalytic experiments

First the reaction was conducted in the absence of any catalyst but appropriate amounts of hydrogen peroxide. There was no activity observed as shown in Figure S8. In the presence of catalyst, the conversion of morin was observed by the disappearance of the peak at  $\lambda = 410$  nm and appearance of a new absorption peak around  $\lambda = 320$  nm over time (see Figure 5(a) and (b)). Kinetic measurements revealed *pseudo*-first order kinetics of the catalytic oxidation of morin with excess peroxide with respect to the concentration of morin for both the pure cobalt oxide and the doped catalysts. This assumption seemed justified by the linearity of the natural logarithmic plots against time shown in Figure 5(c). Interestingly, all dopants had a negative effect on the catalytic activity of the cobalt oxide as the apparent rates decreased upon doping. Amongst the dopants, potassium proved to be the worst as apparent rates decreased significantly. On the other hand, cesium was a better dopant, showing a high rate compared to other dopants. The apparent rates increased with increasing concentrations of the catalysts, as shown in Figure 5(d) and in Figure S9. However, the slope from a differential analysis (see Figure S10 in ESI) revealed a fractional order with respect to active metal in the range of 0.2 (for pure Co<sub>3</sub>O<sub>4</sub>) to 0.7 (for Mg/Co<sub>3</sub>O<sub>4</sub>). This rather low value for the dependency of effective rate with concentration of active metal could be a hint for the mass transport of morin to the active sites limiting the overall reaction.



Figure 5: (a) Time-based spectral evolution of morin oxidation measured at time intervals of three minutes. (b) Kinetic traces for catalyzed oxidation of morin monitored at  $\lambda = 410$  nm. (c) Natural logarithmic plots for the determination of reaction order. (d) Dependence of apparent rate constants on the Co<sub>3</sub>O<sub>4</sub> concentration monitored at  $\lambda = 410$  nm. Reaction conditions:  $1 \times 10^{-3}$  M of morin,  $10 \times 10^{-3}$  M of H<sub>2</sub>O<sub>2</sub> and  $6.9 \times 10^{-6}$  M catalyst (In graph d the concentration of the catalyst was varied)

Such mass transport limited reactions are often encountered in heterogeneously catalyzed reactions [28]. A-priori criteria are a common technique to estimate the influence of mass transport based on only a few preliminary experimental data. Here, we used the well-established Weisz-Prater criterion to assign the influence of pore diffusion limitations.

$$\Phi = \frac{r_{eff} \cdot R^2}{c_s \cdot D_{eff}} \tag{1}$$

As indicated in Equation (1), the criterion requires the effective reaction rate  $r_{eff}$ , the known catalyst pellet radius R, substrate concentration  $c_s$  (assuming no film diffusion limitation) and the effective Diffusion coefficient  $D_{eff}$ . The effective diffusion coefficient was estimated from literature data of the molecular diffusion coefficient of morin in water to be  $5.45 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> (see SI for details). With particle pellet sizes in the range of 5 µm, the Weisz-Prater criterion resulted in value well below 0.1 for all catalyst tested (see Supporting Information for details). This is in agreement with the fractional order of catalyst concentration. This indicates that the metal oxide catalysts are highly active for the oxidation reaction and although the pellet size is small, this high intrinsic activity results in the diffusion through the pores of the catalyst to be the overall rate limiting step.

Lithium doped cobalt oxide was chosen for catalyst recyclability and reusability tests because it allowed the detection of both Co and Li via ICP-MS to account for possible metal leaching. The lithium doped cobalt oxide was recycled using a centrifuge and reusability tests revealed only a minor decrease in conversion from the second to the fourth run as shown in Figure 7. Interestingly, the first catalytic run appeared to be slower than the second to fourth runs. This can be attributed to surface restructuring of the catalyst during the first catalytic cycle resulting in a slower reaction. To further account for this, the second , third and fourth catalytic runs gave reactions rate constants of 8.9, 9.2 and  $8.8 \times 10^{-4}$  min<sup>-1</sup>, respectively. These values do not differ significantly from each other compared to  $6.61 \times 10^{-4}$  min<sup>-1</sup> from the first catalytic cycle. The similar reaction rate constants up to the fourth catalytic run are an indication of good catalytic stability. It even seems that the catalyst required some induction period through the first run to become fully active. The small difference in activity correlated with the leaching test using ICP-MS, as they indicated that there was no detectable leaching of either Li nor Co ions from the catalytic material (ICP-MS detection limit of 1 ppm). This illustrates the good stability of the material in catalytic conditions set out in this work.

This behavior was also reported in literature for the reduction of 4-nitrophenol with similar catalysts [7].



**Figure 7:** Catalyst reusability study using the Li/Co<sub>3</sub>O<sub>4</sub> catalysts showing slight changes in apparent reaction rate constants with each catalytic cycle. Reaction conditions:  $2 \times 10^{-3}$  M of morin,  $10 \times 10^{-3}$  M of H<sub>2</sub>O<sub>2</sub> and  $21 \times 10^{-6}$  M catalyst.

#### Discussions

The surface properties of the synthesized cobalt oxide and the alkali- and alkaline-earth metal doped cobalt oxide show the mesoporous nature as depicted by the type IV hysteresis loops. The type IV hysteresis loops are similar to the one reported by Wu *et al.* [29]. This mesoporous nature of the materials is brought about by the structure-directing inverse micelles that form by the P-123 surfactant. Also the use of nitric acid to induce acidic media played a crucial role. Literature results indicate that the NO<sub>x</sub> species formed by decomposition of nitrate ions are adsorbed on the surface of oxo-clusters, and thus, prevent condensation of the clusters [18].

The effect of the dopants on  $Co_3O_4$  is significant on the surface properties such as surface area and pore characteristics. The alkaline earth metals induce a relatively small reduction of the surface area compared to the alkali counterparts. Also changes in pore volume of the undoped  $Co_3O_4$  are consistent with the above trend. The alkaline earth metal dopants reduced the pores of  $Co_3O_4$  considerably less than the alkali earth metals. These results are consistent with literature and are mostly due to increases in crystallite sizes upon doping, see table 1 [30].

Furthermore, the sol-gel method used in the synthesis of the cobalt oxide yielded spinel cobalt oxide structure. The presence of  $Co^{3+}$  and  $Co^{2+}$  in the cobalt oxide structure is indicative of

different reactive sites and thus different binding energy between the cations with different oxidation states and lattice oxygen of the oxide. The binding of oxygen to different cobalt species is evidenced by two reduction peaks in temperature-programmed reduction. The first peak that appeared is assigned to the most electropositive cobalt cation due to ease of reduction. Changes in electronic structure upon doping changed the electronic environment around the cationic centers, evidenced by shifting of reduction peaks in H<sub>2</sub>-TPR measurements, Figure 3a, and shifting binding energy in XPS (see Table S2 in supplementary information). These two methods are complementing each other. In XPS analysis, an increase of electron density around the cationic center is observed. This phenomenon is also observed in H<sub>2</sub>-TPR analysis.

The slight reduction in catalytic activity of Co<sub>3</sub>O<sub>4</sub> upon doping is not surprising. The decreased surface area of the Co<sub>3</sub>O<sub>4</sub> upon doping is the major contributing factor because changes in the electronic structure of the original oxide as depicted by H<sub>2</sub>-TPR measurements and XPS are minimal. However, even minimal changes in chemical and physical environment of the pure Co<sub>3</sub>O<sub>4</sub>, can play a role in the catalytic activity of this material. The shifting of reduction peaks to higher temperatures, indicative of a change in electronic environment on the catalyst surface, does not lead to improved catalytic activity in oxidation reactions. The less reducibility of the catalyst is an indication of a poor oxidation catalyst [18]. Also the increase in basicity of the catalyst upon doping is an indication of less adsorption of morin on the catalysts surface. Morin is a polyphenolic compound, thus it has many basic hydroxyl moieties which adsorb better on acid sites. Furthermore, we recently showed that mesoporous cobalt oxide is a good reduction catalysts using the reduction of 4-nitrophenol as a model reaction [31]. In our recent publication, we also reported other active transition metal oxides including cobalt oxide in 4-nitrophenol reduction [32]. Changes in the electronic structure of the catalytically active metal oxide supports upon immobilization of AuPd nanoalloys was the main reason for improved catalytic activity. Herein, this change in electronic structure is also evident in the XPS analysis, Figure 3b, where there is an extra component on the O 1s core level electrons indicative of a different electron environment compared to the undoped catalyst.

It is important to note that the negative effect the alkaline earth metal dopants have in the electronic structure, as shown by significant shifts to higher temperature compared to the alkali counterparts in the H<sub>2</sub>-TPR measurements, Figure 3, is countered by the better surface areas they

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posses. While on the other hand, the smaller surface areas of the alkali doped Co<sub>3</sub>O<sub>4</sub> catalyst is countered by the better reducibility when compared to the alkaline earth metal doped Co<sub>3</sub>O<sub>4</sub> catalysts. This might be one of the reasons for similar activities observed for the doped catalysts. It is, however, not the first time that doping with alkali and alkaline earth metals decrease catalytic activity in oxidation reaction. Elkins *et al.* reported decrease in activity of MgO catalyst in oxidative coupling of methane upon doping with Li [33].

#### Conclusion

The synthesis, characterization and catalytic activity of pure and alkali- and alkaline earth metal doped-Co<sub>3</sub>O<sub>4</sub> was successfully described. Furthermore, the incorporation of doping agents did not change the morphology of the mesoporous cobalt oxide. The catalytic activity of the assynthesized catalyst decreased upon doping and based on the H<sub>2</sub>-TPR and XPS analysis electronic properties were altered. Textural properties also play a significant role in determining the catalytic activity.

Furthermore, comparison of the doped catalysts amongst themselves illustrate that the basicity of the dopant plays a crucial role in the activity as more basic dopants result in higher reaction rates in the oxidation of morin. All the catalyst are very active for oxidation of morin. In addition, Co is a less expensive metal compared to noble metals such as Pt and Au. Therefore, these catalysts have a potential to replace noble-metal-based catalysts.

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