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#### Article

## Improved and Reduced Performance of Cu- and Ni-Substituted $Co_3O_4$ Catalysts with Varying $Co_{Oh}/Co_{Td}$ and $Co^{3+}/Co^{2+}$ Ratios for the **Complete Catalytic Oxidation of VOCs**

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(MMOFs) retained similar spinel structures but exhibited improved and reduced performance for o-xylene oxidation, respectively. Physicochemical characterization and DFT calculations revealed that Cu and Ni substitution into the  $Co_3O_4$  spinel varied the valence  $(Co^{3+}/Co^{2+})$  and geometry  $(Co_{Oh}/Co_{Td})$  distributions of Co cations through different partial electron transfer and substitution sites. The higher Co<sup>3+</sup>/Co<sup>2+</sup> and  $Co_{Oh}/Co_{Td}$  ratios of the  $CuCo_2O_4$  catalyst contributed to the superior



reducibility and oxygen mobility, which facilitated the oxidation of intermediates at lower temperatures in the catalytic oxidation of o-xylene. Meanwhile, the NiCo<sub>2</sub>O<sub>4</sub> catalyst with lower Co<sup>3+</sup>/Co<sup>2+</sup> and Co<sub>Oh</sub>/Co<sub>Td</sub> ratios could not completely oxidize intermediates under the same conditions due to inferior redox properties. Therefore, the  $CuCo_2O_4$  catalyst showed superior catalytic activity and stability to the NiCo2O4 catalyst for the catalytic oxidation of o-xylene. This work provides insights into the synthesis of substituted  $Co_3O_4$  catalysts from MMOFs and mechanism of substituting effects, which might guide the design of efficient TMO catalysts for VOC treatment.

**KEYWORDS:**  $Co_3O_4$  spinel, substituting effects,  $Co^{3+}/Co^{2+}$ ,  $Co_{Oh}/Co_{Td}$ , VOCs, MMOFs

#### 1. INTRODUCTION

Volatile organic compounds (VOCs) discharged from industrial production, building finishing, and transportation have become some of the most challenging pollutants since most of them are highly toxic for human health, and play an important role in the formation of photochemical smog, secondary aerosols, and ozone pollution.<sup>1,2</sup> The catalytic oxidation of VOCs is generally regarded as one of the most promising treatments for VOC pollution.<sup>3,4</sup> Especially, the resourceful transition metal oxide (TMO) catalysts, which could mineralize VOCs into CO2 and H2O at relatively low temperatures, have attracted extensive attention on account of their effectiveness and economic advantages.<sup>5,6</sup>

The  $Co_3O_4$  spinel with the  $AB_2O_4$  structure, one tetrahedral  $Co^{2+}$  in the A site and two octahedral  $Co^{3+}$  in the B site, is one of the most investigated TMOs in the catalytic oxidation of VOCs.<sup>7-10</sup> Substituting effects are usually utilized to improve the catalytic performance of the  $Co_3O_4$  spinel.<sup>11-13</sup> Zheng et al. replaced  $\text{Co}^{2+}$  of  $\text{Co}_3\text{O}_4$  nanowires with  $\text{Cu}^{2+}$ , which showed a much higher catalytic activity for CO oxidation due to the favorable formation of oxygen vacancies in the  $\mathrm{Co}^{3+} O-Cu^{2+}$  bonding than in  $Co^{3+}-O-Co^{2+}$ .<sup>14</sup> Wang et al. reported that Ni substitution boosted the catalytic oxidation of acetone over Co<sub>3</sub>O<sub>4</sub> hollow mesoporous spheres, which was attributed to different defective sites and reducibility.<sup>15</sup> However, unchanging and even inhibiting effects of Cu and Ni substitution on the performance of the Co<sub>3</sub>O<sub>4</sub> catalyst due to different preparation methods and substituting sites and amounts were also presented in literatures.<sup>16,17</sup> More importantly, the formation and mechanism of substituting effects still remain ambiguous. It is necessary and valuable to systematically explore the substituted Co<sub>3</sub>O<sub>4</sub> catalysts for promoting the catalytic oxidation of VOCs.

Recently, metal-organic frameworks (MOFs) were employed to prepare TMO catalysts owing to the high specific surface area, special topology, and tunable preparation.<sup>18-20</sup> These TMO catalysts inherited the properties of original MOFs, exhibiting excellent performance in catalysis and other

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Figure 1. (a) TGA curves of the original MMOFs, and (b) XRD patterns, (c) Raman spectra, and (d) synthesis scheme of MCo<sub>2</sub>O<sub>4</sub> catalysts.

Table 1. Composition and Textural Parameters of MCo<sub>2</sub>O<sub>4</sub> Catalysts

sample	M/Co (molar)	Co 2p <sub>3/2</sub> Co <sup>3+</sup> /Co <sup>2+</sup>	$\begin{array}{c} Cu \ 2p_{3/2} \\ Cu^+/Cu^{2+} \end{array}$	Cu LMM <sup>a</sup> Cu <sup>+</sup> /Cu <sup>2+</sup>	Ni 2p <sub>3/2</sub> Ni <sup>3+</sup> /Ni <sup>2+</sup>	$S_{\rm BET}^{b}$ (m <sup>2</sup> /g)	$V_{\rm p}^{\ c} \ ({\rm cm}^3/{\rm g})$	$D_{\mathrm{P}}^{d}$ (nm)
Co <sub>3</sub> O <sub>4</sub>	1:2	1.53				35.9	0.19	22.60
CuCo <sub>2</sub> O <sub>4</sub>	1.08:1.92	1.58	0.43	0.50		22.4	0.12	22.06
NiCo <sub>2</sub> O <sub>4</sub>	1.04:1.96	1.44			0.92	58.5	0.20	14.53
<sup>a</sup> Cu LMM Aug	ger spectrum. <sup>b</sup> BET	surface area. <sup>c</sup> I	Pore volume. <sup>d</sup>	Average pore di	ameter.			

fields. In our previous work, Co<sub>3</sub>O<sub>4</sub> catalysts with different shapes derived from MOFs obviously enhanced the catalytic oxidation of o-xylene, and the crucial mechanism was also successfully disclosed, eliminating the effects of different preparation methods.<sup>21</sup> What's more, mixed MOFs (MMOFs) and their derivatives have showed better catalytic performance due to the synergism of multiple metals.<sup>22,23</sup> Jia et al. prepared bimetal oxide CuO/Co<sub>3</sub>O<sub>4</sub> catalysts through the pyrolysis of the Cu<sup>2+</sup> substituted ZIF-67 precursor, which promoted the catalytic oxidation of toluene prior to CuO and Co<sub>3</sub>O<sub>4</sub> catalysts because of the high mutual dispersion of two oxides.<sup>24</sup> Therefore, MMOFs with multiple metals dispersed in the structure could serve as the precursors of substituted Co<sub>3</sub>O<sub>4</sub> catalysts, and their substituting behaviors and catalytic mechanism would be further unveiled based on the uniform preparation method.

Herein, we prepared Cu- and Ni-substituted  $Co_3O_4$  catalysts through the pyrolysis of MMOFs, which retained the spinel phase and adopted similar microstructures. *o*-Xylene was taken as the target VOC for catalytic evaluation. The substituting sites and amounts, valence and geometry distributions, and redox properties of substituted catalysts were investigated through designed experiments combined with DFT calculations. A mechanism for the improved and reduced performance of Cu- and Ni-substituted  $Co_3O_4$  catalysts in the catalytic oxidation of *o*-xylene was eventually proposed.

#### 2. EXPERIMENTAL SECTION

Cu- and Ni-substituted  $Co_3O_4$  ( $CuCo_2O_4$  and  $NiCo_2O_4$ ) catalysts were synthesized through the pyrolysis of  $CuCo_2$ -ZIF-9 and  $NiCo_2$ -ZIF-9 precursors, respectively. Pure  $Co_3O_4$ , CuO, and NiO and other substituted catalysts with different molar ratios were also prepared for reference. More preparation details, details of catalytic activity evaluation, and methods of catalyst characterization and DFT calculations are shown in the Supporting Information. Additionally,  $Co_3O_4$ ,  $CuCo_2O_4$ , and  $NiCo_2O_4$  are abbreviated as  $MCo_2O_4$  (M = Co, Cu, and Ni) in this work.

#### 3. RESULTS AND DISCUSSION

**3.1. Catalyst Derivation from MMOFs.** The thermogravimetric analysis (TGA) in Figure 1a indicates that Cu and Ni substitution did not evidently change the stability of ZIF-9 precursors, and Cu- and Ni-substituted  $Co_3O_4$  catalysts were derived from MMOFs at 350 °C without further loss at higher temperatures. XRD patterns (Figure 1b) show that the crystal structure of MCo<sub>2</sub>O<sub>4</sub> consists of the spinel phase (JCPDS No. 42-1467) with the space group of *Fd-3m* (227).<sup>12</sup> Additionally, minor impurities of CuO and NiO were observed in CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>, respectively, but their effects on the catalytic oxidation of *o*-xylene could be excluded due to much lower activities (Figure S1).<sup>15,17</sup> Raman spectra of MCo<sub>2</sub>O<sub>4</sub> in Figure 1c also confirm their main spinel structure with  $A_{1er} E_{er} F_{2er}^2$ ,  $F_{2er}^2$ 



Figure 2. (a,b) Catalytic activity, (c) stability, (d) and specific reaction rate (inset: Ea) of  $MCo_2O_4$  catalysts in *o*-xylene oxidation (reaction conditions: [*o*-xylene] = 150 ppm,  $Q = 100 \text{ mL/min} (N_2/O_2 = 4:1)$ ).

and  $F_{2g}^3$  modes, respectively, and the slight red-shift is related to the residual stress and lattice distortion after Cu and Ni substitution into the Co<sub>3</sub>O<sub>4</sub> spinel.<sup>15,25</sup> The actual M/Co ratio (Table 1) was also identified to match with the nominal 1:2 by ICP-OES. Therefore, Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts have been successfully prepared through the pyrolysis of MMOFs as shown in the synthesis scheme (Figure 1d).

**3.2. Catalytic Performance.** The catalytic performance of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> was evaluated via o-xylene oxidation in the temperature range of 200–320  $\,^\circ C$  with WHSV = 120,000 mL/( $g\cdot h$ ) (Figure 2a,b). It is notable that Cu substitution obviously promoted the catalytic oxidation of o-xylene. The  $T_{50\%}$  and  $T_{90\%}$  of o-xylene conversion and  $\mathrm{CO}_2$ yield (280 °C) for CuCo<sub>2</sub>O<sub>4</sub> could reach 252 °C, 273 °C, and 100%, respectively. However, Ni substitution tremendously inhibited the catalytic oxidation of *o*-xylene. The values of  $T_{50\%}$  $T_{90\%}$  and CO<sub>2</sub> yield (280 °C) for NiCo<sub>2</sub>O<sub>4</sub> are 283 °C, 298 °C, and 44%, respectively. In addition, Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts with other molar ratios also displayed similar improved and reduced performance, respectively (Figure S2). The continuous on-stream tests in Figure 2c describe that MCo<sub>2</sub>O<sub>4</sub> catalysts maintained stable o-xylene conversion at 280 °C, but the conversion decreased at 260 °C over Co<sub>3</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> catalysts due to the more incomplete oxidation and occupied active sites.<sup>26,27</sup> Therefore, Cu and Ni substitution improved and reduced the catalytic activity and

stability of the  $Co_3O_4$  catalyst, respectively. The changing catalytic performance probably results from different substitution sites and amounts, which would be further discussed in the following analyses for the sake of efficient substituted  $Co_3O_4$  catalysts.

Kinetic measurements were conducted at higher WHSV =  $1.2 \times 10^6 \text{ mL/(g·h)}$  to investigate the different performance of CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> catalysts, and the internal diffusion and external diffusion were eliminated in our previous work.<sup>21</sup> Their intrinsic catalytic performance (Figure 2d) in the kinetic region was presented by the specific reaction rate to unit weight and unit surface area based on the textural parameters (Table 1) and dosage of catalysts. The higher and lower specific reaction rates suggest the superior and inferior intrinsic catalytic performance of CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>, respectively. The apparent activation energies (Ea) calculated from the linear Arrhenius plots (Figure S3) are 62.0, 100.2, and 133.9 kJ/mol for CuCo2O4, Co3O4, and NiCo2O4 catalysts, respectively. The lower Ea usually means the easier activation of molecules at the same temperature; thus, the catalytic oxidation of o-xylene over MCo<sub>2</sub>O<sub>4</sub> probably proceeds in this order:  $CuCo_2O_4 > Co_3O_4 > NiCo_2O_4$ . Consequently, Cu and Ni substitution into the Co<sub>3</sub>O<sub>4</sub> catalyst not only altered the total catalytic performance but also affected the intrinsic catalytic performance and apparent activation energy for oxylene oxidation.



Figure 3. Normalized XANES and EXAFS spectra of (a,d) Co-K edge, (b,e) Cu-K edge, and (c,f) Ni-K edge in MCo<sub>2</sub>O<sub>4</sub> catalysts.

**3.3. Textural Properties.** The N<sub>2</sub> adsorption-desorption isotherms of MCo<sub>2</sub>O<sub>4</sub> catalysts shown in Figure S4a are close to the typical type IV isotherm with a hysteresis loop type H3 based on the IUPAC, suggesting the existence of mesopores.<sup>29</sup> Similarly, their pore size distribution curves also center at the mesoporous region in Figure S4b. These results indicate that Cu- and Ni-substituted  $Co_3O_4$  catalysts still maintain a mesoporous structure. The calculated specific surface area and porosity of MCo<sub>2</sub>O<sub>4</sub> in Table 1 follow this order: NiCo<sub>2</sub>O<sub>4</sub>  $> Co_3O_4 > CuCo_2O_4$ , which might not be the main reason for the improved and reduced performance of Cu- and Nisubstituted Co<sub>3</sub>O<sub>4</sub> catalysts. TEM images (Figure S5a,d,e,h) depict that both CuCo2O4 and NiCo2O4 are composed of aggregated nanoparticles and Cu, Ni, and Co are homogeneously distributed in their elemental mapping (Figure S5b,c,f,g). Additionally, lattice spacings of 0.451 and 0.450

nm are observed in HRTEM images (Figure S5d,f inset) of  $CuCo_2O_4$  and  $NiCo_2O_4$ , which correspond to the (111) plane of the spinel structure.<sup>8,30</sup> A similar lattice spacing associated with the (111) plane is also shown in the HRTEM image of  $Co_3O_4$  (Figure S6c), indicating that Cu and Ni substitution did not appreciably change the lattice structure of the  $Co_3O_4$  nanoparticles. Therefore,  $CuCo_2O_4$  and  $NiCo_2O_4$  maintained similar spinel phase and mesoporous and lattice structures to  $Co_3O_4$ .

**3.4. Surface Chemical States.** The surface chemical states of Cu- and Ni-substituted  $Co_3O_4$  catalysts were analyzed by X-ray photoelectron spectroscopy (XPS). Co 2p spectra in Figure S7a display two main peaks at 779.7 and 794.7 eV corresponding to Co  $2p_{3/2}$  and Co  $2p_{1/2}$  spin-orbit doublets.<sup>9,31</sup> Co  $2p_{3/2}$  and Co  $2p_{1/2}$  peaks were further deconvoluted into  $Co^{3+}$  (779.7 ± 0.2 and 794.6 ± 0.2 eV) and



Figure 4. The (a-c) spinel structure, (d-f) charge density contour plots, (g-i) projected density of states (PDOS), and (j-1) schematic of the Co d-band center and O p-band center of MCo<sub>2</sub>O<sub>4</sub> catalysts.

 $\text{Co}^{2+}$  (781.4 ± 0.2 and 796.3 ± 0.2 eV) peaks, respectively.<sup>31</sup> The deconvolution results (Table 1) show that the Co<sup>3+</sup>/Co<sup>2+</sup> ratio follows this sequence: CuCo<sub>2</sub>O<sub>4</sub> > Co<sub>3</sub>O<sub>4</sub> > NiCo<sub>2</sub>O<sub>4</sub>, which might be one of the reasons for the improved and reduced performance of Cu- and Ni-substitution Co<sub>3</sub>O<sub>4</sub> catalysts. A high Co<sup>3+</sup>/Co<sup>2+</sup> ratio usually gives rise to good reducibility, contributing to the catalytic oxidation of VOCs over MCo<sub>2</sub>O<sub>4</sub> catalysts.<sup>32,33</sup>

To figure out the effects of Cu and Ni substitution on the  $Co^{3+}/Co^{2+}$  ratio, Cu  $2p_{3/2}$ , Cu LMM, and Ni  $2p_{3/2}$  spectra were investigated. The Cu  $2p_{3/2}$  spectrum of CuCo<sub>2</sub>O<sub>4</sub> in Figure S7b consisted of Cu<sup>+</sup> and Cu<sup>2+</sup> peaks at 932.9 and 934.3 eV and satellite peaks at 941.1 and 943.5 eV, respectively.<sup>34,35</sup> The Cu LMM Auger spectrum (Figure S7c) further confirmed the distribution of Cu<sup>+</sup> and Cu<sup>2+</sup> with two corresponding peaks at 913.1 and 917.9 eV.<sup>36</sup> Their deconvolution results in Table 1 indicate that  $\mathrm{Cu}^{2+}$  are the main  $\mathrm{Cu}$  species in  $\mathrm{Cu}\mathrm{Co}_2\mathrm{O}_4$ accompanied with  $\mathrm{Cu}^{\scriptscriptstyle +}.$  The presence of  $\mathrm{Cu}^{\scriptscriptstyle +}$  might be ascribed to the stronger electronic affinity of  $Cu^{2+}$  (1.49) than  $Co^{2+}$ (1.38), resulting in the partial electron transfer from  $Co^{2+}$  to Cu<sup>2+</sup> through the adjacent lattice oxygen.<sup>37,38</sup> Meanwhile, more Co<sup>3+</sup> accordingly formed through the indirect electron transfer, leading to the increased  $Co^{3+}/Co^{2+}$  ratio. Moreover, the Ni 2p<sub>3/2</sub> spectra of NiCo<sub>2</sub>O<sub>4</sub> in Figure S7d could be divided into three peaks at 854.2, 856.1, and 861.2 eV, consistent with the characteristics of Ni2+, Ni3+, and the satellite peak.<sup>39–41</sup> The deconvolution results in Table 1 show the coexistence of Ni<sup>2+</sup> and Ni<sup>3+</sup>, which possibly arose from the partial electron transfer from  $Ni^{2+}$  (1.37) to more electrophilic  $\text{Co}^{3+}$  (1.69) through the adjacent lattice oxygen.<sup>38,42</sup> Thus, more  $\text{Co}^{2+}$  accordingly formed through the indirect electron transfer, causing the decreased  $\text{Co}^{3+}/\text{Co}^{2+}$  ratio.

3.5. Cation Distribution. X-ray adsorption near-edge structure (XANES) spectra were measured to further elucidate the valence distribution of  $MCo_2O_4$  catalysts. According to the position of the Co-K edge in Figure 3a, the valence state of Co cations follows this order:  $CuCo_2O_4 > Co_3O_4 > NiCo_2O_4$ indicating the increased  $Co^{3+}/Co^{2+}$  ratio in  $CuCo_2O_4$  and decreased  $Co^{3+}/Co^{2+}$  ratio in NiCo<sub>2</sub>O<sub>4</sub><sup>43</sup> Similarly, the valence state of Cu cations in CuCo<sub>2</sub>O<sub>4</sub> is lower than that in CuO as shown by the position of the Cu-K edge in Figure 3b, which means the presence of low-valence Cu cations in CuCo<sub>2</sub>O<sub>4</sub>; the valence state of Ni cations in NiCo<sub>2</sub>O<sub>4</sub> is higher than that in NiO based on the position of the Ni-K edge in Figure 3c, which suggests the presence of high-valence Ni cations in  $NiCo_2O_4^{42,44}$  The existence of low-valence Cu cations and high-valence Ni cations in MCo2O4 demonstrates the partial electron transfer between Cu(Ni) cations and Co cations through the adjacent lattice oxygen, which might be one of reasons for the increased (decreased) Co<sup>3+</sup>/Co<sup>2+</sup> ratios and varying performance of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts. The XANES results are consistent with the XPS analysis with regard to the surface chemical states of MCo<sub>2</sub>O<sub>4</sub> catalysts.

The geometry distribution of  $MCo_2O_4$  catalysts was also explored by extended X-ray absorption fine structure (EXAFS) spectra analysis. All radial distances in Figure 3 are the apparent distance with a difference of 0.3-0.4 Å to the real

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Figure 5. Profiles of (a) CO-TPR and (b) O2-TPD and (c,d) oxygen vacancy formation for MCO2O4 catalysts.

bond distance. There are three typical peaks in the EXAFS spectra of Co-K edge (Figure 3d): the first peaks below 2 Å are assigned to Co-O shell, scattering from the nearest neighbor lattice oxygen around the absorbing atoms; the peaks at  $\sim$ 2.5 Å correspond to the Co<sub>Oh</sub>-M<sub>Oh</sub> shell, scattering from the metal cation to the closest neighbor metal cations around octahedral sites; the peaks at ~3.0 Å are related to the  $Co_{Td}-M_{Ob}/M_{Td}$ shell, scattering from the metal cation to the closest neighbor metal cations around tetrahedral sites.<sup>43,45</sup> These results reveal that Co cations are distributed in both the octahedral and tetrahedral sites of MCo2O4. Similarly, the CuOh-MOh and  $Cu_{Td}\text{-}M_{Oh}/M_{Td}$  shells at ~2.5 and ~3.0 Å (Figure 3e) suggest that Cu cations are also distributed in both the octahedral and tetrahedral sites of CuCo<sub>2</sub>O<sub>4</sub>.<sup>13,44</sup> Meanwhile, the single Ni<sub>Ob</sub>- $M_{Oh}$  shell at ~2.5 Å (Figure 3f) manifests that Ni cations are only distributed in octahedral sites of  $NiCo_2O_4$ .<sup>13,46</sup> Therefore, Ni substitution to  $\text{Co}_{\text{Oh}}$  sites of the  $\text{Co}_3\text{O}_4$  spinel reduced the Co<sub>Oh</sub>/Co<sub>Td</sub> ratio in NiCo<sub>2</sub>O<sub>4</sub>, but equal amounts of Cu substitution to both  $Co_{Oh}$  and  $Co_{Td}$  sites of the  $Co_3O_4$  spinel brought about a higher  $Co_{Oh}/Co_{Td}$  ratio in  $CuCo_2O_4$ .

The first Co-O shells at the Co-K edge for  $MCo_2O_4$  catalysts were further fitted in R-space (Figure S8). The  $Co_{Oh}/Co_{Td}$ ratio could also be calculated through the fitting coordination numbers of the Co-O shells according to the hexa-coordinate  $Co_{Oh}$ -O and tetra-coordinate  $Co_{Td}$ -O in the spinel structure. Table S1 shows that the  $Co_{Oh}/Co_{Td}$  ratio for  $Co_3O_4$ ,  $CuCo_2O_4$ , and  $NiCo_2O_4$  is 2.03, 2.39, and 1.11, respectively, demonstrating the increased and decreased  $Co_{Oh}/Co_{Td}$  ratio of Cu- and Ni-substituted  $Co_3O_4$  catalysts.<sup>47,48</sup> There are also  $A_{1g}$ and  $F_{2g}^1$  modes associated with the vibration of  $CoO_6$  octahedrons and CoO<sub>4</sub> tetrahedrons in the Raman spectra of MCo<sub>2</sub>O<sub>4</sub>, and the intensity ratio of A<sub>1g</sub>/F<sup>1</sup><sub>2g</sub> confirmed that the Co<sub>Oh</sub>/Co<sub>Td</sub> ratio followed this sequence: CuCo<sub>2</sub>O<sub>4</sub> > Co<sub>3</sub>O<sub>4</sub> > NiCo<sub>2</sub>O<sub>4</sub>.<sup>25</sup> Octahedral Co sites of the Co<sub>3</sub>O<sub>4</sub> spinel have been suggested to be more active in the catalytic oxidation of VOCs considering their open framework and effective hybridization with oxygen through strong  $\sigma$  interaction, which is beneficial for electron transfer in redox cycles.<sup>49,50</sup>

3.6. Electronic Structures. Electronic structure analyses were performed through DFT calculations to investigate the changed  $Co^{3+}/Co^{2+}$  and  $Co_{Oh}/Co_{Td}$  ratios in  $MCo_2O_4$ catalysts. Their simulated structure as presented in Figure 4a-c retained the spinel phase with the space group of Fd-3m (227) according to experimental results. The higher charge density of Cu atoms and lower charge density of Co atoms in CuCo<sub>2</sub>O<sub>4</sub> (Figure 4e) indicate the partial electron transfer from Co to Cu atoms through adjacent oxygen atoms. Similarly, the higher charge density of Co atoms and lower charge density of Ni atoms in NiCo<sub>2</sub>O<sub>4</sub> (Figure 4f) display the partial electron transfer from Ni to Co atoms through adjacent oxygen atoms. The charge density of MCo2O4 was also presented in the form of the Bader charge (Table S2), which is a description of the atomic charge, associated to ionic valence but lower than it due to the partial covalency of the M-O bond.<sup>51,52</sup> The Bader charge of Co atoms in MCo<sub>2</sub>O<sub>4</sub> follows this order:  $CuCo_2O_4$  (+1.40lel) >  $Co_3O_4$  (+1.38lel) >  $NiCo_2O_4$  (+1.34lel), confirming the different partial electron transfer occurring in Cu and Ni substitution. Accordingly, Cu and Ni atoms gave charges of +1.14lel and + 1.22lel in  $CuCo_2O_4$  and  $NiCo_2O_4$ , respectively. Thus, theoretical



Figure 6. In situ DRIFTS and mass spectra for the oxidation of adsorbed *o*-xylene over (a,d)  $CuCo_2O_4$ , (b,e)  $Co_3O_4$ , and (c,f)  $NiCo_2O_4$  catalysts (reaction conditions: [*o*-xylene] = 150 ppm, Q = 100 mL/min).

calculations unraveled the different partial electron transfer as well, which generated the increased and decreased  $\rm Co^{3+}/\rm Co^{2+}$  ratios of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub>.

The projected density of states (PDOS) on Co, Cu, Ni, and O elements for MCo<sub>2</sub>O<sub>4</sub> catalysts was calculated and plotted in Figure 4g-i to analyze the interaction between M 3d orbitals and O 2p orbitals. In general, Co 3d, Cu 3d, and Ni 3d orbitals are strongly hybridized with O 2p orbitals in both valence and conduction bands, implying the partial covalency of the M-O bond for MCo<sub>2</sub>O<sub>4</sub><sup>48,53</sup> The covalent character or overlap between Co 3d and O 2p states in the spinel has been considered to be associated with their redox properties and catalytic performance.<sup>43,46</sup> Thus, the Co d-band center and O p-band center of MCo<sub>2</sub>O<sub>4</sub> were computed, for which a lower energy difference indicates a higher Co-O covalency.<sup>46,54</sup> As shown in Figure 4j-l and Table S2, the value of ICo d-O pl follows this sequence:  $CuCo_2O_4$  (0.88 eV) <  $Co_3O_4$  (0.98 eV) < NiCo<sub>2</sub>O<sub>4</sub> (1.00 eV). A higher Co<sub>Oh</sub>/Co<sub>Td</sub> ratio enhanced the Co-O covalency of MCo<sub>2</sub>O<sub>4</sub> catalysts because of the stronger  $\sigma$  interaction of Co<sub>Oh</sub>-O orbitals than the  $\pi$  interaction of Co<sub>Td</sub>-O orbitals. Moreover, the greater Co-O covalency could facilitate the electron transfer between Co cations and O anions and thereby enhance catalytic performance, which might account for the improved and reduced performance of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts with different Co<sub>Ob</sub>/ Co<sub>Td</sub> ratios.

3.7. Redox Properties. The reducibility of Cu- and Nisubstituted Co<sub>3</sub>O<sub>4</sub> catalysts was studied through CO-TPR measurements in Figure 5a. Two main peaks were exhibited in the reduction of MCo2O4 by 5 vol % CO/Ar flow: for CuCo<sub>2</sub>O<sub>4</sub>, the sharp peak at 174 °C is assigned to the reduction of  $Cu^{2+}(Cu^{+})$  to  $Cu^{0}$ , and the broad peak at higher temperatures represents the successive reduction of  $Co^{3^+} \rightarrow Co^{2^+} \rightarrow Co^0$ ;<sup>35,36</sup> for NiCo<sub>2</sub>O<sub>4</sub>, the sharp peak at 251 °C is associated with the reduction of Co<sup>3+</sup> to Co<sup>2+</sup>, and the broad peak at higher temperatures shows the successive reduction of  $Ni^{3+}(Ni^{2+}) \rightarrow Ni^{0}$  and  $Co^{2+} \rightarrow Co^{0}; 55, 56$  for  $Co_{3}O_{4}$ , the sharp peak at 255 °C is related to the reduction of Co<sup>3+</sup> to Co<sup>2+</sup>, and the broad peak at higher temperatures describes the reduction of  $Co^{2+}$  to  $Co^{0.15}$ . The whole reduction profile of  $CuCo_2O_4$ shifted to lower temperatures compared with Co<sub>3</sub>O<sub>4</sub>, revealing the better reducibility after Cu substitution; the much weaker reduction peak of Co<sup>3+</sup> to Co<sup>2+</sup> in the NiCo<sub>2</sub>O<sub>4</sub> profile also indicates its worse reducibility after Ni substitution to Co<sub>3</sub>O<sub>4</sub>.

The oxygen mobility over  $MCo_2O_4$  catalysts was analyzed through  $O_2$ -TPD experiments and theoretical calculations. In the full  $O_2$ -TPD profiles (Figure S9), the strong peaks at temperatures higher than 700 °C are associated with the liberation of bulk lattice oxygen species, which are considered to be inactive in the catalytic oxidation of VOCs.<sup>10,12</sup> In their amplified profiles at lower temperatures (Figure 5b), two other kinds of oxygen species are observed: the peaks around 160 °C



Figure 7. Schematic for the improved and reduced performance of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts in o-xylene oxidation.

relate to the desorption of adsorbed oxygen species (O<sub>ads</sub>), and the peaks at 321, 344, and 386 °C correspond to the desorption of surface lattice oxygen species (O<sub>lat</sub>).<sup>57</sup> These oxygen species desorbed at temperatures lower than 450 °C usually serve as the reactive oxygen species (ROS) in the catalytic oxidation of VOCs.<sup>10,12</sup> The increased desorption of O<sub>ads</sub> might benefit the incomplete oxidation of *o*-xylene into intermediates, contributing to the higher activity of the Co<sub>3</sub>O<sub>4</sub> catalyst than substituted catalysts at light-off temperatures. However, Cu and Ni substitution obviously affected the desorption of surface Olat, which is decisive to the complete catalytic oxidation of o-xylene. The surface Olat of CuCo2O4 desorbed at lower temperatures indicates the better oxygen mobility of the catalyst, which could easily interact with reactants and form oxygen vacancy, promoting the catalytic oxidation of o-xylene. Likewise, the higher desorption temperature for NiCo<sub>2</sub>O<sub>4</sub> means worse oxygen mobility, inhibiting the catalytic oxidation with o-xylene.

What's more, the energy for removing oxygen atom and forming oxygen vacancy ( $E_{Ov}$ ) on the simulated MCo<sub>2</sub>O<sub>4</sub> (111) surface (Figure S10) was also calculated as shown in Figure 5c,d and Table S3. The  $E_{Ov}$  follows this sequence: CuCo<sub>2</sub>O<sub>4</sub> < Co<sub>3</sub>O<sub>4</sub> < NiCo<sub>2</sub>O<sub>4</sub>, which theoretically revealed the different oxygen mobility of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts. Thus, Cu and Ni substitution into Co<sub>3</sub>O<sub>4</sub> influences the reducibility and oxygen mobility through the different distributions of Co cations in valence and geometry and finally gives rise to the improved and reduced performance of CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> catalysts in *o*-xylene oxidation.

**3.8. In Situ DRIFTS Study.** The adsorption and oxidation behaviors of *o*-xylene over Cu- and Ni-substituted  $Co_3O_4$  catalysts were recorded through in situ DRIFTS. Meanwhile, outlet gases were analyzed by mass spectra. When *o*-xylene/N<sub>2</sub> was introduced into the sample chamber at 160 °C, the stretching vibration  $\nu$ (C–H) of –CH at 3068 cm<sup>-1</sup> and skeleton stretching vibration of the aromatic ring at 1600–1200 cm<sup>-1</sup> were observed (Figure S11), implying the existence

of adsorbed *o*-xylene on the catalyst surface.<sup>58</sup> During the continuous adsorption, intermediates including alkoxide species at 1139 cm<sup>-1</sup>; aldehyde species at 1664 cm<sup>-1</sup>; carboxylate species at 1574, 1542, 1415, and 1410 cm<sup>-1</sup>; and anhydride species at 1237 cm<sup>-1</sup> successively appeared and increased through the interaction of methyl groups with ROS on the catalyst surface.<sup>33,59</sup> The mass spectra of outlet gases exhibit that no other organic byproducts were detected except  $CO_2$  and residual *o*-xylene. When reactant gases were changed to air, the cleavage of aromatic ring and the disappearance of intermediates were subsequently achieved at 280 °C, and no other organic byproducts were detected except the  $CO_2$  product in the mass spectra of outlet gases (Figure 6).

In the adsorption and oxidation of o-xylene, alkoxide and carboxylate species appeared as main intermediates in the in situ DRIFTS for all MCo2O4 catalysts, but aldehyde and anhydride species were observed over Co3O4, which might hinder the catalytic oxidation of intermediates.<sup>57</sup> Specifically, the intensity of intermediates over CuCo<sub>2</sub>O<sub>4</sub> increased to the highest level at 160 °C and displayed a decrease at 200 °C during the oxidation of adsorbed o-xylene (Figure 6a), while the corresponding reactions for Co<sub>3</sub>O<sub>4</sub> occurred at 200 and 240 °C, respectively (Figure 6b). The formation and consumption of intermediates at lower temperatures signify that CuCo<sub>2</sub>O<sub>4</sub> promoted the catalytic oxidation of intermediates without extra accumulation. Additionally, the peaks of carboxylate species over NiCo2O4 in Figure 6c did not completely disappear under the same conditions when all intermediates over Co3O4 and CuCo2O4 have been oxidized into CO<sub>2</sub> and H<sub>2</sub>O at 280 °C. It is revealed that the catalytic oxidation of carboxylate species over NiCo<sub>2</sub>O<sub>4</sub> was partly inhibited, although other intermediates were not hindered. Therefore, Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts promoted and inhibited the catalytic oxidation of intermediates, respectively, which probably originated from their different redox properties due to the changes of  $Co^{3+}/Co^{2+}$  and  $Co_{Ob}/$  $Co_{Td}$  ratios in Cu and Ni substitution into  $Co_3O_4$ .

**3.9. Catalytic Mechanism.** A possible mechanism for the improved and reduced performance of Cu- and Ni-substituted  $Co_3O_4$  catalysts in *o*-xylene oxidation is proposed in Figure 7. First, CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> with a spinel structure were derived from MMOFs: Cu replaced both Co<sub>Oh</sub> and Co<sub>Td</sub> sites, but Ni only took the place of Co<sub>Oh</sub> sites. The different substitution sites led to the higher and lower  $Co_{Ob}/Co_{Td}$  ratios for  $CuCo_2O_4$  and  $NiCo_2O_4$ , respectively. The partial electron transfer between Cu(Ni) and Co cations through the adjacent lattice oxygen also increased and decreased  $Co^{3+}/Co^{2+}$  ratios for CuCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>. High Co<sub>Oh</sub>/Co<sub>Td</sub> and Co<sup>3+</sup>/Co<sup>2+</sup> ratios have generally been supposed to be associated with the reducibility and oxygen mobility of the Co<sub>3</sub>O<sub>4</sub> spinel, contributing to the superior catalytic performance for VOC combustion.<sup>33,49</sup> Therefore, the different replacement sites and electron interactions of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> varied the distribution of Co<sub>Oh</sub> and Co<sup>3+</sup> in geometry and valence, which further affected their redox properties for the catalytic oxidation of o-xylene: CuCo2O4 displayed improved performance through the lower-temperature oxidation of intermediates including alkoxide and carboxylate species without the accumulation of aldehyde and anhydride species; NiCo2O4 presented reduced performance through the incomplete oxidation of carboxylate species under the same conditions.

#### 4. IMPLICATIONS

In this work, Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts derived from MMOF precursors exhibited improved and reduced performance for o-xylene oxidation, although they retained the spinel phase and similar textural parameters. The improved catalytic performance of CuCo2O4 arises from the increased  $Co_{Oh}/Co_{Td}$  ratio in Cu substitution to both  $Co_{Oh}$  and  $Co_{Td}$ sites and the higher Co<sup>3+</sup>/Co<sup>2+</sup> ratio owing to the partial electron transfer between Cu and Co cations through the adjacent lattice oxygen, which contribute to good reducibility and oxygen mobility. Likewise, the only substitution of Ni to Co<sub>Ob</sub> sites and partial electron transfer between Ni and Co cations decreased  $Co_{Ob}/Co_{Td}$  and  $Co^{3+}/Co^{2+}$  ratios, which reduced the catalytic performance of NiCo2O4 for o-xylene oxidation. Specifically, intermediates over CuCo<sub>2</sub>O<sub>4</sub> including alkoxide and carboxylate species were promptly formed and oxidized at lower temperatures without extra accumulation, while those over NiCo<sub>2</sub>O<sub>4</sub> were not completely oxidized under the same conditions. When comparing with other reported catalysts for the catalytic oxidation of o-xylene (Table S4), the optimal CuCo<sub>2</sub>O<sub>4</sub> is more active than most TMO catalysts and comparable to some supported noble metal catalysts (Supporting Information). Therefore, this work presents a promising approach to synthesize substituted Co<sub>3</sub>O<sub>4</sub> catalysts from MMOFs and provides insights into the improved and reduced performance of Cu- and Ni-substituted Co<sub>3</sub>O<sub>4</sub> catalysts due to the varying  $Co_{Oh}/Co_{Td}$  and  $Co^{3+}/Co^{2+}$  ratios, which is beneficial for designing efficient TMO catalysts and avoiding the negative effects of substitution in the catalytic oxidation of VOCs.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02450.

Details of catalyst preparation, activity evaluation, characterization, and DFT calculations; catalytic activity

of pure TMO and other substituted  $Co_3O_4$  catalysts; Arrhenius plots; nitrogen adsorption–desorption isotherms and pore size distribution curves; TEM and HRTEM images; XPS and Auger spectra; fitting results of EXAFS spectra; full profiles of  $O_2$ -TPD; in situ DRIFTS of *o*-xylene adsorption; DFT calculated results; and comparison of various catalysts (PDF)

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#### Notes

The authors declare no competing financial interest.

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