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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 Co³⁺/Co²⁺ 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 NiCo₂O₄ catalyst with lower Co³⁺/Co²⁺ and Co_{Oh}/Co_{Td} 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.^{1,2} The catalytic oxidation of VOCs is generally regarded as one of the most promising treatments for VOC pollution.^{3,4} 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.^{5,6}

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.⁷⁻¹⁰ Substituting effects are usually utilized to improve the catalytic performance of the Co_3O_4 spinel.¹¹⁻¹³ Zheng et al. replaced Co^{2+} of Co_3O_4 nanowires with 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 $Co^{3+}-O-Co^{2+}$.¹⁴ Wang et al. reported that Ni substitution boosted the catalytic oxidation of acetone over Co₃O₄ hollow mesoporous spheres, which was attributed to different defective sites and reducibility.¹⁵ However, unchanging and even inhibiting effects of Cu and Ni substitution on the performance of the Co₃O₄ catalyst due to different preparation methods and substituting sites and amounts were also presented in literatures.^{16,17} More importantly, the formation and mechanism of substituting effects still remain ambiguous. It is necessary and valuable to systematically explore the substituted Co₃O₄ 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.¹⁸⁻²⁰ 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 MCo₂O₄ catalysts.

Table 1. Composition and Textural Parameters of MCo₂O₄ Catalysts

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

fields. In our previous work, Co₃O₄ 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.²¹ What's more, mixed MOFs (MMOFs) and their derivatives have showed better catalytic performance due to the synergism of multiple metals.^{22,23} Jia et al. prepared bimetal oxide CuO/Co₃O₄ catalysts through the pyrolysis of the Cu²⁺ substituted ZIF-67 precursor, which promoted the catalytic oxidation of toluene prior to CuO and Co₃O₄ catalysts because of the high mutual dispersion of two oxides.²⁴ Therefore, MMOFs with multiple metals dispersed in the structure could serve as the precursors of substituted Co₃O₄ 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 MCo₂O₄ consists of the spinel phase (JCPDS No. 42-1467) with the space group of *Fd-3m* (227).¹² Additionally, minor impurities of CuO and NiO were observed in CuCo₂O₄ and NiCo₂O₄, respectively, but their effects on the catalytic oxidation of *o*-xylene could be excluded due to much lower activities (Figure S1).^{15,17} Raman spectra of MCo₂O₄ 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 Co₃O₄ spinel.^{15,25} 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 Co₃O₄ 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 Co₃O₄ 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 CO_2 yield (280 °C) for CuCo₂O₄ 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 CO₂ yield (280 °C) for NiCo₂O₄ are 283 °C, 298 °C, and 44%, respectively. In addition, Cu- and Ni-substituted Co₃O₄ 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 MCo₂O₄ catalysts maintained stable o-xylene conversion at 280 °C, but the conversion decreased at 260 °C over Co₃O₄ and NiCo₂O₄ catalysts due to the more incomplete oxidation and occupied active sites.^{26,27} 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 CuCo₂O₄ and NiCo₂O₄ catalysts, and the internal diffusion and external diffusion were eliminated in our previous work.²¹ 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 CuCo₂O₄ and NiCo₂O₄, 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 MCo₂O₄ probably proceeds in this order: $CuCo_2O_4 > Co_3O_4 > NiCo_2O_4$. Consequently, Cu and Ni substitution into the Co₃O₄ 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 MCo₂O₄ catalysts.

3.3. Textural Properties. The N₂ adsorption-desorption isotherms of MCo₂O₄ 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.²⁹ 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 MCo₂O₄ in Table 1 follow this order: NiCo₂O₄ $> Co_3O_4 > CuCo_2O_4$, which might not be the main reason for the improved and reduced performance of Cu- and Nisubstituted Co₃O₄ 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.^{8,30} 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.^{9,31} 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 MCo₂O₄ catalysts.

 Co^{2+} (781.4 ± 0.2 and 796.3 ± 0.2 eV) peaks, respectively.³¹ The deconvolution results (Table 1) show that the Co³⁺/Co²⁺ ratio follows this sequence: CuCo₂O₄ > Co₃O₄ > NiCo₂O₄, which might be one of the reasons for the improved and reduced performance of Cu- and Ni-substitution Co₃O₄ catalysts. A high Co³⁺/Co²⁺ ratio usually gives rise to good reducibility, contributing to the catalytic oxidation of VOCs over MCo₂O₄ catalysts.^{32,33}

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 CuCo₂O₄ in Figure S7b consisted of Cu⁺ and Cu²⁺ peaks at 932.9 and 934.3 eV and satellite peaks at 941.1 and 943.5 eV, respectively.^{34,35} The Cu LMM Auger spectrum (Figure S7c) further confirmed the distribution of Cu⁺ and Cu²⁺ with two corresponding peaks at 913.1 and 917.9 eV.³⁶ Their deconvolution results in Table 1 indicate that Cu^{2+} are the main 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 Cu²⁺ through the adjacent lattice oxygen.^{37,38} Meanwhile, more Co³⁺ accordingly formed through the indirect electron transfer, leading to the increased Co^{3+}/Co^{2+} ratio. Moreover, the Ni 2p_{3/2} spectra of NiCo₂O₄ 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.^{39–41} The deconvolution results in Table 1 show the coexistence of Ni²⁺ and Ni³⁺, which possibly arose from the partial electron transfer from Ni^{2+} (1.37) to more electrophilic Co^{3+} (1.69) through the adjacent lattice oxygen.^{38,42} Thus, more 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 NiCo₂O₄⁴³ Similarly, the valence state of Cu cations in CuCo₂O₄ 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 CuCo₂O₄; the valence state of Ni cations in NiCo₂O₄ 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) Co³⁺/Co²⁺ ratios and varying performance of Cu- and Ni-substituted Co₃O₄ catalysts. The XANES results are consistent with the XPS analysis with regard to the surface chemical states of MCo₂O₄ 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_{Oh}-M_{Oh} 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.^{43,45} 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 CuCo₂O₄.^{13,44} Meanwhile, the single Ni_{Ob}- M_{Oh} shell at ~2.5 Å (Figure 3f) manifests that Ni cations are only distributed in octahedral sites of $NiCo_2O_4$.^{13,46} Therefore, Ni substitution to Co_{Oh} sites of the Co_3O_4 spinel reduced the Co_{Oh}/Co_{Td} ratio in NiCo₂O₄, 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.^{47,48} There are also A_{1g} and F_{2g}^1 modes associated with the vibration of CoO_6 octahedrons and CoO₄ tetrahedrons in the Raman spectra of MCo₂O₄, and the intensity ratio of A_{1g}/F¹_{2g} confirmed that the Co_{Oh}/Co_{Td} ratio followed this sequence: CuCo₂O₄ > Co₃O₄ > NiCo₂O₄.²⁵ Octahedral Co sites of the Co₃O₄ 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 σ interaction, which is beneficial for electron transfer in redox cycles.^{49,50}

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 CuCo₂O₄ (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 NiCo₂O₄ (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.^{51,52} The Bader charge of Co atoms in MCo₂O₄ 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 Co₃O₄.

The projected density of states (PDOS) on Co, Cu, Ni, and O elements for MCo₂O₄ 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 MCo₂O₄^{48,53} 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.^{43,46} Thus, the Co d-band center and O p-band center of MCo₂O₄ were computed, for which a lower energy difference indicates a higher Co-O covalency.^{46,54} 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) < NiCo₂O₄ (1.00 eV). A higher Co_{Oh}/Co_{Td} ratio enhanced the Co-O covalency of MCo₂O₄ catalysts because of the stronger σ interaction of Co_{Oh}-O orbitals than the π interaction of Co_{Td}-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 Co₃O₄ catalysts with different Co_{Ob}/ Co_{Td} ratios.

3.7. Redox Properties. The reducibility of Cu- and Nisubstituted Co₃O₄ 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 CuCo₂O₄, 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 $Co^{3^+} \rightarrow Co^{2^+} \rightarrow Co^0$;^{35,36} for NiCo₂O₄, the sharp peak at 251 °C is associated with the reduction of Co³⁺ to Co²⁺, 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 Co³⁺ to Co²⁺, 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 Co₃O₄, revealing the better reducibility after Cu substitution; the much weaker reduction peak of Co³⁺ to Co²⁺ in the NiCo₂O₄ profile also indicates its worse reducibility after Ni substitution to Co₃O₄.

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.^{10,12} 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 Co₃O₄ catalysts in o-xylene oxidation.

relate to the desorption of adsorbed oxygen species (O_{ads}), and the peaks at 321, 344, and 386 °C correspond to the desorption of surface lattice oxygen species (O_{lat}).⁵⁷ These oxygen species desorbed at temperatures lower than 450 °C usually serve as the reactive oxygen species (ROS) in the catalytic oxidation of VOCs.^{10,12} The increased desorption of O_{ads} might benefit the incomplete oxidation of *o*-xylene into intermediates, contributing to the higher activity of the Co₃O₄ 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 NiCo₂O₄ 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 MCo₂O₄ (111) surface (Figure S10) was also calculated as shown in Figure 5c,d and Table S3. The E_{Ov} follows this sequence: CuCo₂O₄ < Co₃O₄ < NiCo₂O₄, which theoretically revealed the different oxygen mobility of Cu- and Ni-substituted Co₃O₄ catalysts. Thus, Cu and Ni substitution into Co₃O₄ 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 CuCo₂O₄ and NiCo₂O₄ 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/N₂ was introduced into the sample chamber at 160 °C, the stretching vibration ν (C–H) of –CH at 3068 cm⁻¹ and skeleton stretching vibration of the aromatic ring at 1600–1200 cm⁻¹ were observed (Figure S11), implying the existence

of adsorbed *o*-xylene on the catalyst surface.⁵⁸ During the continuous adsorption, intermediates including alkoxide species at 1139 cm⁻¹; aldehyde species at 1664 cm⁻¹; carboxylate species at 1574, 1542, 1415, and 1410 cm⁻¹; and anhydride species at 1237 cm⁻¹ successively appeared and increased through the interaction of methyl groups with ROS on the catalyst surface.^{33,59} 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.⁵⁷ Specifically, the intensity of intermediates over CuCo₂O₄ 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 Co₃O₄ occurred at 200 and 240 °C, respectively (Figure 6b). The formation and consumption of intermediates at lower temperatures signify that CuCo₂O₄ 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 CO₂ and H₂O at 280 °C. It is revealed that the catalytic oxidation of carboxylate species over NiCo₂O₄ was partly inhibited, although other intermediates were not hindered. Therefore, Cu- and Ni-substituted Co₃O₄ 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, CuCo₂O₄ and NiCo₂O₄ with a spinel structure were derived from MMOFs: Cu replaced both Co_{Oh} and Co_{Td} sites, but Ni only took the place of Co_{Oh} 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 CuCo₂O₄ and NiCo₂O₄. High Co_{Oh}/Co_{Td} and Co³⁺/Co²⁺ ratios have generally been supposed to be associated with the reducibility and oxygen mobility of the Co₃O₄ spinel, contributing to the superior catalytic performance for VOC combustion.^{33,49} Therefore, the different replacement sites and electron interactions of Cu- and Ni-substituted Co₃O₄ varied the distribution of Co_{Oh} and Co³⁺ 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 Co₃O₄ 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 Co³⁺/Co²⁺ 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_{Ob} 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 CuCo₂O₄ including alkoxide and carboxylate species were promptly formed and oxidized at lower temperatures without extra accumulation, while those over NiCo₂O₄ 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 CuCo₂O₄ 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 Co₃O₄ catalysts from MMOFs and provides insights into the improved and reduced performance of Cu- and Ni-substituted Co₃O₄ 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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