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# Macroscopic Hexagonal Co<sub>3</sub>O<sub>4</sub> Tubes Derived from Controllable Two-Dimensional Metal-Organic Layer Single Crystals: Formation Mechanism and Catalytic Activity

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crystal transformation was spontaneous at 393 K. Further addition of MeCN as an interference agent eventually leads to the formation of macroscopic hexagonal tubes. Among all of the as-synthesized  $Co_3O_4$ , Co-MeCN-O with a hexagonal tube morphology exhibited the best catalytic performance in toluene oxidation, it achieved a toluene conversion of 90% ( $T_{90}$ ) at ~227 °C (a space velocity of 60 000 mL g<sup>-1</sup> h<sup>-1</sup>) and the activity energy ( $E_a$ ) is 69.5 kJ mol<sup>-1</sup>. A series of characterizations were performed to investigate the structure–activity correlation. It was found that there are more structure defects, more adsorbed surface oxygen species, more surface  $Co^{3+}$  species, and higher reducibility at low temperatures on the Co-MeCN-O than on other  $Co_3O_4$  samples; these factors are responsible for its excellent catalytic performance. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization showed that, when there is no oxygen in the atmosphere, the lattice oxygen may be involved in the activation of toluene, and the gas-phase oxygen replenished by the oxygen vacancies was essential for the total oxidation of toluene on the surface of the Co-MeCN-O catalysts, it also proves the importance of oxygen vacancies. Moreover, for the Co-MeCN-O catalysts, no obvious decrease in catalytic performance was observed after 120 h at 220 °C and it is still stable after cycling tests, which indicates that it exhibits excellent stability for toluene oxidation. This study sheds lights on the controllable synthesis of macroporous–microporous materials in single-crystalline form without an external template, and, thus, it may serve as a reference for future design and synthesis of hollow porous materials with outstanding catalytic performance.

# 1. INTRODUCTION

 $Co_3O_4$  materials, because of their low-cost and interesting physical and chemical properties, have been studied for many applications, such as water oxidation, carbon monoxide (CO) oxidation, and catalytic oxidation of volatile organic compounds (VOCs).<sup>1–9</sup> The morphology of  $Co_3O_4$  plays a vital role in catalysis<sup>10–13</sup> and can vary with reagrd to different preparation methods, such as hydrothermal methods,<sup>13</sup> sol–gel methods,<sup>5</sup> template methods,<sup>14</sup> coprecipitation methods,<sup>15</sup> and so on. Even though researchers are still exploring new ways to synthesize  $Co_3O_4$  with unique structures for better catalytic performance.

inner crystallites-were identified as playing a key role in the

formation of the unique hollow structure. The calculated change in Gibbs free energy ( $\Delta G = -1.18$  eV) indicated that the crystal-to-

Recently, it was found that metal oxides prepared using metal-organic framework (MOF) pyrolysis exhibit unique physicochemical properties and are advantageous for the catalytic oxidation of VOCs, in terms of activity and selectivity.<sup>16,17</sup> Compared with metal oxides prepared via traditional routes, the MOFs-derived metal oxide materials generally have advantages such as larger surface area, higher porosity, controllable morphology, and homogeneous heter-oatom doping, which are considered to be crucial for catalysis.<sup>18–23</sup> Furthermore, the pyrolysis of MOFs could easily lead to the formation of hollow-structured metal oxides,

and outer grown

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which favors rapid mass transport, because of their hierarchical porous structures and high density of metal sites.<sup>24–28</sup>

The synthesis strategies of hollow-structured materials derived from MOFs can be sorted into two categories, namely, the pyrolysis of hollow-structured MOFs into hollow oxides, and the directional conversion to hollow oxides from assynthesized MOFs with predesigned morphology and composition.<sup>27</sup> Typical synthetic routes include gradually dissolution-regrowth, template-mediated assembly, interfacial ion exchange, selective etching, self-catalytic pyrolysis, and heterogeneous contraction.<sup>29–35</sup> Recently, Shen et al.<sup>36</sup> reported the ordered and highly oriented macropores within MOFs single crystal, opening up a new area, namely, threedimensional (3D)-ordered materials containing both macropores and micropores. The ordered macroporous-microporous structure was synthesized by the template of polystyrene nanosphere and a heterogeneous double-solventinduced nucleation method. This hierarchical framework improved mass-diffusion properties and showed superior catalytic activity, relative to the other ZIF-8 catalysts. The synthesis of mesoporous or macroporous hierarchical crystalline porous materials remains an important goal;<sup>37,38</sup> the typical synthetic routes of the hollow structure have been studied very clearly, but in single-crystalline form, they are still difficult to design and synthesize.

Herein, we report the a controllable synthesis of macroscopic hexagonal  $Co_3O_4$  tubes derived from two-dimensional (2D) MOLs single crystals and discuss the formation process of the unique hollow structure. Different interference solvents are used in the hydrothermal synthesis process, leading to  $Co_3O_4$  with different morphologies after templates pyrolysis. When MeCN is introduced as an interference solvent, the macroscopic hexagonal tubes form and the entire 3D hollowmorphology MOFs remained monocrystalline. We performed time-dependent experiments to track the formation mechanism of the hollow morphology. The catalytic oxidation of toluene is also studied and the hollow-morphology  $Co_3O_4$  showed a better performance than other  $Co_3O_4$  derived from other 2D MOLs.

#### 2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. All chemicals were used without further purification in this work, and all of them are analytical grade. All of the MOF templates were prepared through hydrothermal conditions but in different solvents. In a typical method, 2 mmol 3,5pyridinedicarboxylate (HPYDC) and 5 mmol NaOH were dissolved in 60 mL of mixture of H2O and acetonitrile (MeCN)\N,Ndimethylformamide (DMF)\ethanol (EtOH)\H2O\methanol (MeO-H)\isopropanol (IPA)\ethylene glycol (EG) with a 1:1 ratio, 4 mmol  $Co(NO_3)_2 \cdot 6H_2O$  was dissolved in 20 mL of the same mixture of solvents. These two solvents were mixed and a lot of pink powder came out. Then, stirring was performed for 5 min and the resulting mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave. We then held the temperature at 120 °C for 72 h in an electric oven. After heat preservation, the autoclave was cooled to room temperature in the natural environment. Afterward, the red crystals were collected after washing with ethanol several times and dried at 80 °C for 12 h. The products that came from different solvents were named Co-MeCN, Co-DMF, Co-EtOH, Co-H<sub>2</sub>O, Co-MeOH, Co-IPA, and Co-EG, respectively.

Further products were made from the above-mentioned crystals through a two-stage calcination method. First, they are calcined in  $N_2$  at a heating ramp of 2 °C min<sup>-1</sup> from 30 °C to 500 °C and held for 5 h. Then they were cooled naturally to room temperature, calcined in dry air from room temperature to 350 °C at a heating ramp of 2 °C

min<sup>-1</sup>, and held for 5 h. The final products were called Co-MeCN-O, Co-DMF-O, Co-EtOH-O, Co-H<sub>2</sub>O-O, Co-MeOH-O, Co-IPA-O, and Co-EG-O, respectively.

**2.2. Catalyst Characterization.** Physicochemical properties of these cobalt-based compounds and oxides were measured via various techniques, including XRD, SEM, BET, H<sub>2</sub>-TPR, O<sub>2</sub>-TPD, XPS, and in situ DRIFTS. The detailed characterization procedures are described in the Supporting Information.

**2.3. Catalytic Evaluations.** The catalytic activity of toluene oxidation over all the cobalt oxides was evaluated in a tubular fixedbed microreactor system ( $\Phi = 10.0 \text{ mm}$ ). The feeding gas contains 1000 ppm toluene and 20%O<sub>2</sub>/N<sub>2</sub>, with a weight hourly space velocity (WHSV) of 60 000 mL g<sup>-1</sup> h<sup>-1</sup> in the testing process. The specific test conditions are described in the Supporting Information.

#### 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Structural Characterization.** Figure 1 illustrates the preparation of MOFs-derived Co<sub>3</sub>O<sub>4</sub> schemati-



**Figure 1.** Schematic illustrations of the synthesis process for the MOFs-derived  $Co_3O_4$ : (a) molecular structure of 3,5-pyridinedicarboxylic and  $Co(NO_3)_2$  acid, (b) the  $CoNO_6$  decahedron 2D MOLs are yellow polyhedral and the topology is 6,<sup>3</sup> and (c) stacking of the 2D MOLs by hydrogen-bonding interactions (dashed bonds). (d) Typical SEM images of as-synthesized  $Co_3O_4$ .

cally, and all the Co<sub>3</sub>O<sub>4</sub> samples were similarly prepared. Specifically, the 2D MOL templates were synthesized through a typically hydrothermal method, and its structure was identified previously by X-ray single-crystal diffraction as  $[Co(3,5-pydc)(H_2O)_2]_n$  (Figures 1a and 1b).<sup>39,40</sup> During synthesis, sodium hydrate was used to assist ligand dehydrogenation. Briefly, 3,5-pyridinedicarboxylic acid with double molar  $Co(NO_3)_2 \cdot 6H_2O$  were mixed in solution, immediately forming a pink powder of [Co(3,5-pydc)- $(H_2O)_2]_n$  when no interference agent is present or the interference agent is ethanol, methanol, N,N-dimethylformamide, isopropanol, or ethylene glycol. However, when acetonitrile was used as an interference agent, a crystalline powder of  $[{Co(3,5-pydc)(H_2O)_4} \cdot H_2O]_n$  was obtained (see Figure S1 in the Supporting Information).<sup>41</sup> After maintaining at 120 °C for 72 h, the color of the crystalline powder changed from pink to red. The corresponding crystal structures are shown in Figures 1b and 1c. The thermogravimetric analyses (TGA) result shows that the structure frame was collapsed at 350 °C in the nitrogen atmosphere and lost most components after 500 °C (see Figures S2a and S2b in the Supporting Information). Therefore, after two-stage calcination, the MOF template was removed and Co<sub>3</sub>O<sub>4</sub> was harvested (see Figure 1d).

The as-obtained products were investigated via powder Xray diffraction (PXRD) to confirm their structural properties. Figure 2a shows that these MOFs templates retained as



Figure 2. PXRD patterns of (a) the MOFs templates and (b) the  $Co_3O_4$  products.

crystalline  $[Co(3,5-pydc)(H_2O)_2]_n$ . Because we avoided grinding all of the samples, the discrepancies of peak intensities is derived from the preferential orientation, so that we can ensure their structural integrity. Figure 2b shows that all the products after two-stage calcinations display diffraction peaks at similar positions and with similar relative intensities. The reflections at ~19.0°, 31.4°, 36.7°, 38.5°, 44.9°, 59.3°, and 65.1° correspond to the different planes of the spinel Co<sub>3</sub>O<sub>4</sub> phase (space group: Fdm (No. 227), JCPDS Card No. 42–1467), including (111), (220), (311), (222), (400), (511), and (440).<sup>42,43</sup> No peaks were observed from other Co<sub>3</sub>O<sub>4</sub> phases, proving that all of the  $Co_3O_4$  products have a spinel  $Co_3O_4$  phase. The crystallite size was calculated according to the (311) diffraction peak using the Scherrer equation, and all the results are summarized in Table 1.44 It shows that all of the products have a relatively similar size, in the range of 10-16 nm.

Scanning electron microscopy (SEM) studies were performed to investigate the different morphology of the products. As shown in Figure 3, two-stage calcination did not change the morphologies of the samples. In addition, it can be clearly observed that the Co-H<sub>2</sub>O sample and Co-H<sub>2</sub>O-O sample exhibited four-edge strip morphology (panels a1 and a2 in Figure 3). When EtOH was added as an interference agent, the four-edge strip morphology was retained, but the aspect ratio was increased (panels b1 and b2 in Figure 3). The products became hexagonal prisms (panels c1 and c2 in Figure 3) when DMF was added, and macroscopic hexagonal tubes with a pore size of ~100  $\mu$ m were obtained when MeCN was used as an interference agent (see panels d1, d2, c1, and c2 in Figure 3). During synthesis, we can observe that the building block coordination polymers (CPs) in the form of crystalline powders were constructed in the solvent immediately when the ligand and the metal ions were mixed. As we know, the



Figure 3. SEM images of the as-synthesized MOFs templates and  $Co_3O_4$  samples: (a1) Co-H<sub>2</sub>O, (b1) Co-EtOH, (c1) Co-DMF, (d1) Co-MeCN, (a2) Co-H<sub>2</sub>O-O, (b2) Co-EtOH-O, (c2) Co-DMF-O, (d2) Co-MeCN-O, (e1) Co-MeCN, and (e2) Co-MeCN-O.

water has the strongest polarity in common solvents, when we add some other polarity solvent as the interference agent, the certain crystalline planes of the CPs could selectively absorb them and adjust the morphology by anisotropic growth.<sup>41</sup> It is suggested that the stronger polarity of the interference agent caused greater variation in morphology of the CPs. In addition,

Table 1. Textural Properties, Crystallite Size, and Conversion of Toluene on the Different Co<sub>3</sub>O<sub>4</sub> Samples

sample	pore volume $(cm^3 g^{-1})$	surface area $(m^2 g^{-1})$	crystallite size (nm)	T <sub>50%</sub> (°C)	T <sub>90%</sub> (°C)	$Co^{3+}/(Co^{3+} + Co^{2+})$ (%)	$O_{ads} / (O_{ads} + O_{latt}) $ (%)
Co-MeCN-O	0.41	123.84	10.70	214	227	56.64	57.08
Co-H <sub>2</sub> O-O	0.43	160.08	11.81	231	238	55.49	56.84
Co-EtOH-O	0.35	93.80	10.81	224	241	54.72	54.24
Co-DMF-O	0.42	116.98	12.90	248	258	54.36	43.78



**Figure 4.** Time-dependent crystal growth of Co-MeCN. (a) SEM images and photographs of the powder collected after different growth times. (b) PXRD patterns of the powder collected after different growth times. (c) Diagram of the hollow structure formation process.

we also tried MeOH, EG, and IPA as the interference solvents. The MeOH had nearly the same polarity of EtOH and showed almost the same result (see Figure S3a in the Supporting Information). The weak polarity solvent IPA and nonpolar solvent EG showed little influence of the morphology (see Figures S3b and S3c in the Supporting Information).

3.2. Formation Mechanism of the Macroscopic **Hexagonal Tubes.** When the MeCN became an interference agent, the morphology became macroscopic hexagonal tubes with infrequent micrometer-sized super hollow holes. The single-crystal structure shows that the structure had no changes, even becoming macroscopic hexagonal tubes (see Table S1 in the Supporting Information). To the best of our knowledge, this is the largest macroscopic hexagonal tube morphology that has been reported.45,46 A time-dependent reaction experiment then was conducted to study how this special morphology formed. The reactants were prepared using a one-pot method and divided into reactors, and solvothermal treatment was used for different periods (1, 2, 4, 8, 12, 24, 72, and 96 h) at 120 °C. Photographs of the solids after centrifugal washing were taken (Figure 4a), as shown in Figure 4a; up to 2 h of reaction, all of the products are pink powder crystals, and after 4 h of reaction, the red crystal is presented. The timedependent PXRD shows that the pink powder crystals represent the crystal of  $[{Co(3,5-pydc)(H_2O)_4} \cdot H_2O]_n$  (1), and the pure red crystal is the crystal of [Co(3,5-pydc)- $(H_2O)_2]_n$  (2) (Figure 4b). As time goes by, there are more and more red crystals but fewer powder crystals. For longer periods up to 96 h, all of the powder crystals disappear and only red crystals are left. The time-dependent PXRD also followed this process. Time-dependent scanningelectron microscopy (SEM) analysis shows that, until 4 h, the morphology is mainly four edge strips  $\sim 1 \,\mu m$  in size (Figure 4a). According to the PXRD analysis, it is the powder crystal of 1 (Figure 4b). After 8 h, the morphology changed to hollow quadrilateral prisms. After 12 h, the hollow quadrilateral prisms became bigger. After 24 h, the hollow quadrilateral prisms changed to hollow hexagonal prisms. As time goes by, the hollow hexagonal prisms became bigger and bigger, the hollow pores also became bigger and

bigger, and even cannot hold the hollow hexagonal prism morphology. Taken together, the reactants transformed from 1 to 2 over time. In the beginning, the ligand and the metal ions were present in high concentration in the reaction solution, and assembled to powder crystals; when 2 started to crystallize, the concentration was very low, so at that time, the ligand and metal ions over 1 play the role of seed to help 2 crystallize on 1. 1 was probably covered by 2 at the beginning, but over time, the inner crystallites of 1 dissolved and migrated out to grow outside as 2. This process provided the original hollow inner surface. The change in Gibbs free energy of the transition from 1 to 2 was calculated via density functional theory (DFT), according to the methods described in the Supporting Information. The DFT calculation result is  $\Delta G = -1.18$  eV, which suggested that the reaction was spontaneous at 393 K; this is consistent with the observed results. At the same time, since the entire system tends toward the low-energy state, the process of inner crystallites 2 dissolve and outside crystallites grow, also following this trend.<sup>26</sup> At that moment, certain crystalline facets of 2 were selectively absorbing the interference agent MeCN and adjusting the morphology to macroscopic hexagonal tubes. To support this, we designed an experiment, after the pink powder crystals came out, the solid and the mother liquid were separated by filtering, then the solid was washed by mixed solution (MeCN: $H_2O = 1:1$ ) several times to remove the ligand and metal ions, then transferred 80 mL of the same mixed solution to a Teflon-lined autoclave; the mother liquid was also put into the Teflon-lined autoclave and both of them were heated at 120 °C for 72 h. SEM analysis of the as-synthesized products shows that, without the mother liquid, the powder crystals cannot form a hollow hexagonal prism structure; in another autoclave, with only mother liquid, only a few red crystals can be found and also cannot form the hollow hexagonal prism structure (see Figure S4 in the Supporting Information). Therefore, in this reaction, the formation mechanism of the hollow structure was divided into two simultaneous paths: one is the process of crystal-to-crystal transformation in the solution, which provided the original hollow inner surface, and the other one

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is the process of inner crystallites dissolving and migrating out to grow outside to reduce surface energy. Both paths are indispensable. Their combined action with MeCN eventually led to the formation of macroscopic hexagonal tubes. This formation process provides a proposal on the controllable synthesis of macroporous-microporous materials in singlecrystalline form without an external template, and thus may serve as reference for the design and synthesis of hollow porous materials.

**3.3. Physicochemical Characterization and Catalytic Performance.** After two-stage calcination, the MOFs were changed to  $Co_3O_4$ , with the respective morphology largely retained. Multiple characterization techniques were used to examine the physical and chemical properties of the assynthesized  $Co_3O_4$ , and the catalytic performance of  $Co_3O_4$ was evaluated using toluene oxidation as a model reaction.

The N<sub>2</sub> adsorption–desorption isotherms and pore size distributions of the prepared  $Co_3O_4$  samples are shown in Figure S5 in the Supporting Information. All of the samples display typical hysteresis loops and classical type-IV isotherms, showing that all the  $Co_3O_4$  samples exist mesoporous structures.<sup>47</sup> The BET area and pore volume are summarized in Table 1. The pore volume of all the samples is ~0.40 cm<sup>3</sup> g<sup>-1</sup>, and the specific surface area is in the range of 93.80–160.08 m<sup>2</sup> g<sup>-1</sup>. All of the  $Co_3O_4$  samples exhibits higher specific surface area and pore volume than the traditional  $Co_3O_4$  catalysts; the higher specific area and pore volume indicate more reaction area and is more conducive to the adsorption of reactants.

X-ray photoelectron spectroscopy (XPS) was used to analyze the oxidation states and the surface compositions of the  $Co_3O_4$  samples. As shown in Figure 5a, the Co  $2p_{3/2}$ spectra at ~780.0 eV could be further deconvoluted into two component peaks and two shakeup satellite peaks: the shoulder peak at ~779.9  $\pm$  0.1 eV is associated with Co<sup>3+</sup> and the peak at ~781.4  $\pm$  0.1 eV is associated with Co<sup>2+</sup>, while the peak at 784.8  $\pm$  0.1 eV corresponds to the shakeup satellite peaks of  $Co^{3+}$  and the peak at 789.3  $\pm$  0.1 eV corresponds to the shakeup satellite peaks of  $Co^{2+}$ .<sup>4,48</sup> The O 1s spectra at ~529.9 eV can be deconvoluted into three peaks: at ~529.8 eV, corresponding to surface lattice oxygen  $(O_{latt})$  species; at 531.2 eV, corresponding to surface-adsorbed oxygen (O<sub>ads</sub>) species; and at 533.1 eV, corresponding to chemisorbed water  $(O_w)\!.^{12,49}$  Quantitative analyses via integrating the areas of fitted peaks of the Co  $2p_{3/2}$  and O 1s spectra obtained the relative atomic ratios of  $Co^{3+}/(Co^{3+} + Co^{2+})$  and  $O_{ads}/(O_{ads} + Co^{2+})$ O<sub>latt</sub>) on the surface (see Table 1). Both ratios follow the order Co-MeCN-O > Co-H<sub>2</sub>O-O > Co-EtOH-O > Co-DMF-O. According to previous studies,<sup>8,50,51</sup> more surface  $O_{ads}$  often means more surface oxygen vacancies, in which the increased Co<sup>3+</sup> concentration can impact oxygen desorption, further impacting the catalytic performance. To verify the presence of oxygen vacancies, electron spin resonance (ESR) measurements were performed. As shown in Figure S6 in the Supporting Information, in comparison with other Co<sub>3</sub>O<sub>4</sub>, the Co-MeCN-O showed a stronger signal at g = 2.004, which can be attributed to the oxygen vacancy of nanomaterials.<sup>52</sup> It is expected that the Co-MeCN-O sample with the most surface Co<sup>3+</sup> and O<sub>ads</sub> will lead to more oxygen vacancies, which may exhibit the best catalytic performance among all of the Co<sub>3</sub>O<sub>4</sub> samples (see Figure S7 and Table S2 in the Supporting Information).



Figure 5. XPS spectra of different  $Co_3O_4$  catalysts: (a) Co 2P and (b) O 1s.

Raman scattering was used to study the defects; the Raman spectra of the Co<sub>3</sub>O<sub>4</sub> catalysts are shown in Figure S8 in the Supporting Information.<sup>53</sup> Five different Raman bands can be observed  $(A_{1g} + E_g + 3F_{2g})$  at 194, 472, 514, 610, and 680 cm<sup>-1</sup> in the 100–850 cm<sup>-1</sup> range, corresponding to the different modes of crystalline Co<sub>3</sub>O<sub>4</sub>.<sup>54</sup> The weak Raman peaks located at 194, 514, and 610 cm<sup>-1</sup> can be associated with tetrahedral sites (CoO<sub>4</sub>) characteristics. The band at 472 cm<sup>-1</sup> is attributed to the  $E_{\rm g}$  symmetry, and the strong band located in 680  $\mbox{cm}^{-1}$  is assigned to the symmetry of  $A_{1g}$  which is attributed to the octahedral sites  $(CoO_6)$  of the  $Co_3O_4$ phase. <sup>53</sup> Furthermore, the  $A_{1g}$  symmetry in the Co-EtOH-O, Co-H<sub>2</sub>O-O, and Co-MeCN-O are located at 673 cm<sup>-1</sup>, 671, and  $663 \text{ cm}^{-1}$ , respectively, and are shifted to a lower wavenumber position than that of Co-DMF-O. Usually, the red-shift in the A<sub>1g</sub> symmetry is induced by a more defective structure of the catalyst, which is beneficial to increase the density of surface oxygen vacancies.<sup>51</sup> According to the Raman results, the abundance of surface oxygen vacancies follows the order Co-MeCN-O > Co-H<sub>2</sub>O-O > Co-EtOH-O > Co-DMF-O, which matches well with the XPS results.<sup>51,55</sup>

Temperature-programmed reduction in  $H_2(H_2$ -TPR) was used to investigate the reducibility of the  $Co_3O_4$  catalysts. As shown in Figure S9a in the Supporting Information, there are two peaks presented in the  $H_2$ -TPR profiles, corresponding to a reduction process with two steps. The first peak centered at ~210 °C is attributed to the reduction from  $Co^{3+}$  to  $Co^{2+}$  and is accompanied by a structural change from  $Co_3O_4$  to CoO. The second peak centered at ~305 °C is associated with the further reduction of CoO to simple elemental cobalt.<sup>51,54</sup> Clearly, the reduction peak at ca. 210 °C of the Co-MeCN-O sample showed higher intensity than the other three samples, indicating a higher concentration of  $Co^{3+}$  ions, inconsistent with the XPS results. The weak peak observed at 85–90 °C for all the samples can be attributed to the surface-active oxygen species on the  $Co_3O_4$  catalysts, suggesting the adsorption of molecular oxygen species by the oxygen vacancies.<sup>54,56</sup> These H<sub>2</sub>-TPR results showed good agreement with the Raman results. All of the above results manifest that the more-adsorbed oxygen species and richer  $Co^{3+}$  concentration of Co-MeCN-O enhanced the reducibility, which corresponds to the XPS results.

Temperature-programmed desorption of  $O_2$  ( $O_2$ -TPD) experiments were used to study the interaction between the Co<sub>3</sub>O<sub>4</sub> surface and adsorbed oxygen species. Generally, there are four different types of oxygen species: oxygen vacancies in adsorption molecular oxygen species (O<sub>v</sub>), oxygen ions adsorbed on the surface  $(O_{ads})$ , lattice oxygen  $(O_{latt,s})$  on the surface, and lattice oxygen in bulk phase (O<sub>latt.b</sub>). The desorption tendency follows the order  $O_v > O_{ads} > O_{latt,s} >$ O<sub>latt,b</sub>.<sup>13,57</sup> As observed in Figure S9b in the Supporting Information, the desorption peaks are roughly divided into regions of <450 °C, 450-700 °C, and >700 °C, which correspond to active oxygen on the surface  $(O_v \text{ and } O_{ads})$ , lattice oxygen on the surface, and lattice oxygen in bulk phase. All of the Co<sub>3</sub>O<sub>4</sub> samples presented three peaks and the peak intensity of Co-MeCN-O sample is greater than that observed for other samples, indicating that the Co-MeCN-O sample has more plentiful surface active oxygen species  $(O_v \text{ and } O_{ads})$ . Usually, the more-intense desorption peaks and lower beginning oxygen desorption temperatures lead to better catalytic performance. Consequently, Co-MeCN-O will have better catalytic activity; the Raman and H2-TPR analyses also support this result.

The relationship between toluene conversion and reaction temperature over different  $Co_3O_4$  catalysts is shown in Figure 6a. The increase in toluene conversion can be clearly observed as the temperature rises and reached 100% at 270 °C over all of the catalysts. The Co-MeCN-O sample shows the best catalytic activity, the  $T_{50}$  value (the temperature for 50% toluene conversion) is 214 °C and the  $T_{90}$  value (the



**Figure 6.** (a) Catalytic performance of the Co<sub>3</sub>O<sub>4</sub> catalysts; (b) Arrhenius plots of the Co<sub>3</sub>O<sub>4</sub> catalysts; (c) results from stability tests of Co-MeCN-O at 220 °C; and (d) results from cycling tests over Co-MeCN-O (toluene oxidation conditions: 1000 ppm toluene, 20 vol % O<sub>2</sub>/N<sub>2</sub>, and WHSV = 60 000 mL g<sup>-1</sup> h<sup>-1</sup>).

temperature for 90% toluene conversion) is 227 °C. In contrast, the toluene conversions are significantly lower at 227 °C, namely, 64.37% for Co-EtOH-O, 35.70% for Co-H<sub>2</sub>O-O, and only 6.18% for Co-DMF-O (see Figure S10 and Table S2 in the Supporting Information). The catalytic performance of Co-MeCN-O is also superior, compared with previously reported pure cobalt-based catalysts (see Table S3 in the Supporting Information). Furthermore, the linear Arrhenius plots of toluene conversion over different catalysts were achieved at a low conversion (<20%). As shown in Figure 6b, the apparent activation energy  $(E_a)$  values of the different samples follow the order Co-DMF-O (128.9 kJ/mol) > Co-EtOH-O (94.5 kJ/mol) > Co-H<sub>2</sub>O-O (84.6 kJ/mol) > Co-MeCN-O (69.5 kJ/mol). Usually, the lower  $E_a$  value exhibits superior catalytic activity, and the results confirm that the Co-MeCN-O sample indicates the highest catalytic activity in toluene combustion. In addition, to verify the stability of the Co-MeCN-O, stability tests (at 220 °C for 120 h) and cycling tests over Co-MeCN-O were performed; the toluene conversion remained at 75% with little change (Figure 6c), and the curves in cycling tests overlapped well after three consecutive tests (Figure 6d). SEM and PXRD analyses were used to observe the catalyst after three reaction cycles. As shown in Figure S11a in the Supporting Information, the morphology of the catalyst remained almost the same. The PXRD of the used catalyst was well retained, and no additional peaks from other species were observed (see Figure S11b in the Supporting Information). The TGA curve of the fresh Co-MeCN-O showed only 3.5% weight loss, which can attributed to the desorption of water (see Figure S12a in the Supporting Information), and the TGA curve of the cycling test sample showed only 0.73% weight loss; from these observations, it can be concluded that the Co-MeCN-O does not easily accumulate carbon during reaction (see Figure S12b in the Supporting Information).

In situ DRIFTS analysis was performed to track the instantaneous composition on the surface of the Co-MeCN-O catalyst, which can study the useful oxygen species and the formed intermediates species in the toluene oxidation process. As shown in Figures 7a and 7b, the Co-MeCN-O exposed in 500 ppm toluene/ $N_2$  or toluene/air at different temperatures. As the temperature rises, various species occurred changes. The band at ~1450–1598 cm<sup>-1</sup> can be ascribed to  $\nu(C=C)$ vibrations of the aromatic rings skeleton, the band at 3070  $cm^{-1}$  can be attributed to the methyl ( $-CH_3$ ) group, and the band at 1025 cm<sup>-1</sup> can be ascribed to vibration of the benzene rings on C-H in-plane bending, indicating that the toluene is adsorbed on the surface of the Co-MeCN-O.58 The bands at 1306 cm<sup>-1</sup> are ascribed to vibrations of methylene ( $-CH_2$ ) groups with C-H bending, indicating that the CH<sub>3</sub> groups from toluene was cracked into methylene and formed benzyl  $(C_6H_5-CH_2)$  on the surface of Co-MeCN-O.<sup>51</sup> The bands at ~1135, 1157, 1177, and 1180 cm<sup>-1</sup> are attributed to the stretching vibrations of C-O from typical alkoxide species  $(C_6H_5-CH_2-O)$ . The band at 1215 and 1234 cm<sup>-1</sup> are ascribed to the stretching vibrations of C-O from the phenolate  $(C_6H_5-OH)$  on the surface.<sup>59</sup> The bands at  $\sim 1652$  cm<sup>-1</sup> are attributed to the stretching vibrations of  $\nu$ (C=O), indicating the generation of benzaldehyde species (C<sub>6</sub>H<sub>5</sub>-CHO). The band at ~1541 cm<sup>-1</sup> is ascribed to the formate species (-COO), suggesting the formation of benzoate species ( $C_6H_5$ -COO), which is the key intermediate during toluene oxidation.<sup>51</sup> As shown in Figures 7a and 7b, on



**Figure 7.** (a, b) In situ DRIFTS results for Co-MeCN-O at different temperatures:  $N_2$  + toluene (panel ((a)) and air + toluene (panel ((b)). (c) Schematic diagram of the important components in toluene degradation.

the surface of Co-MeCN-O, the key intermediates are similar in different atmospheres. During the toluene adsorption process, the key intermediates can be clearly observed and the bands of the key products increased with the rising temperature until 200 °C. In the toluene/N2 conditions, after the temperature is >200 °C, the intensity of key intermediate bands and the toluene showed no obvious change (Figure 7a). However, in contrast, when the gas-phase oxygen was added, the intensity of the toluene and key intermediates decreases as the temperature increases (Figure 7b). The above results show that the lattice oxygen and the gas-phase oxygen in the Co-MeCN-O can both involve the initial activation of toluene, because, on the surface of the catalyst, the gas-phase oxygen species could be reconstituted to the surface lattice oxygen; only gaseous oxygen can be used for the deep oxidation of toluene. On the surface of Co-MeCN-O catalysts, according to the in situ DRIFTS result, the process of toluene catalytic oxidation shows that the Mars-van Krevelen (MvK) mechanism and the Langmuir-Hinshelwood (L-H) mechanism operate at the same time.<sup>60</sup> In addition, the reaction mechanism should mainly follow the pathway shown in Figure 7c: toluene  $\rightarrow$  benzyl radical  $\rightarrow$  benzaldehyde  $\rightarrow$  benzoate  $\rightarrow$ formate species  $\rightarrow$  carbon dioxide and water.<sup>61,62</sup>

Significantly, the catalytic performance of  $Co_3O_4$  is associated with many aspects, such as reducibility, oxygen vacancies, morphology, etc. Generally, the generation of surface oxygen vacancies is the main reason for the defective structure of spinel  $Co_3O_4$ , which often leads to the formation of oxygen species adsorbing on the surface by accelerating the adsorption of molecular  $\rm O_2.^{63}$  Meanwhile, the adsorbed oxygen species on the surface can be easy to desorb and is considered to play the main role in the total oxidation of VOCs.<sup>64</sup> Based on the Raman results (Figure S8) and XPS results (Table 1), it can be concluded that the structural defects and surface adsorbed oxygen species are the reason for the excellent catalytic activity of Co-MeCN-O in toluene oxidation. The result of in situ DRIFTS can indicate that the oxygen vacancies replenished the gas-phase oxygen and played a vital role during the toluene oxidation; it also proves the importance of oxygen vacancies. Furthermore, the low-temperature reducibility of Co-MeCN-O may enhance the catalytic performance.<sup>65</sup> During the reaction, toluene is oxidized along with a transformation from  $Co^{3+}$  and  $Co^{2+}$ .<sup>13</sup> At the same time, the increase in the content of high-valence metal ions promotes the reactivity of oxygen species near the metal ions and the chemical potential.<sup>13</sup> Overall, the oxidation state of cobalt also affects the catalytic performance.<sup>66</sup> According to Raman, H<sub>2</sub>-TPR, and XPS analyses, the excellent catalytic activity of Co-MeCN-O is due to better reducibility and a higher abundance of surface  $Co^{3+}$  among all the  $Co_3O_4$  samples.

#### 4. CONCLUSIONS

In summary, macroscopic hexagonal Co<sub>3</sub>O<sub>4</sub> tubes were successfully synthesized through the thermolysis of hollow 2D MOL single crystals. The hollow 2D MOL single crystals were synthesized via the hydrothermal process, with acetonitrile as the interfering agent. Moreover, based on the time-dependent tracking experiments, a formation mechanism including two complementary paths is first discovered to reveal the formation of hollow single-crystalline 2D MOLs, namely, the crystal-to-crystal transformation in the solution and the dissolution + migration (toward the external surface) + recrystallization of inner crystallites to reduce surface energy. The calculation of the change in Gibbs energy ( $\Delta G = -1.18$ eV) also illustrates that the crystal-to-crystal transformation was spontaneous at 393 K. Under the combined action with MeCN, macroscopic hexagonal tubes can be finally obtained. Among all of the as-synthesized Co<sub>3</sub>O<sub>4</sub>, the Co-MeCN-O hexagonal tube morphology shows the best catalytic performance, with regard to toluene oxidation ( $T_{90} = 227 \text{ °C}$ ,  $E_a = 69.5$ kJ mol<sup>-1</sup>). In addition, for the Co-MeCN-O, the catalytic efficiency has no significant decrease after 120 h at 220 °C, and it is stable after the cycling test. At the same time, Co-MeCN-O also shows a greater number of structure defects, more surface adsorbed oxygen species, lower temperature reducibility, and greater surface Co<sup>3+</sup> concentration. All of these features together lead to better catalytic activity. In addition, the in situ DRIFTS shows that, during the toluene total oxidation, the lattice oxygen on the surface of the catalyst may be involved in the toluene initial activation, but the oxygen vacancies that replenished the gas-phase oxygen played a vital role in the toluene total oxidation; it also proves the importance of oxygen vacancies. Our work provides a proposal on a controllable synthesis of macroporous-microporous materials in single-crystalline form without external template and, therefore, may serve as a reference for the design and synthesis of hollow porous materials in the future. It also provides more selection possibility of catalyst in practical applications.

## ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03396.

Supplemental figures and tables (PDF)

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