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### Article

# Metal–Organic Framework-Confined Single-Site Base-Metal Catalyst for Chemoselective Hydrodeoxygenation of Carbonyls and Alcohols

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**ABSTRACT:** Chemoselective deoxygenation of carbonyls and alcohols using hydrogen by heterogeneous base-metal catalysts is crucial for the sustainable production of fine chemicals and biofuels. We report an aluminum metal–organic framework (DUT-5) node support cobalt(II) hydride, which is a highly chemoselective and recyclable heterogeneous catalyst for deoxygenation of a range of aromatic and aliphatic ketones, aldehydes, and primary and secondary alcohols, including biomass-derived substrates under 1 bar H<sub>2</sub>. The single-site cobalt catalyst (DUT-5-CoH) was easily prepared by postsynthetic metalation of the secondary building units (SBUs) of DUT-5 with CoCl<sub>2</sub> followed by the reaction of NaEt<sub>3</sub>BH. X-ray photoelectron spectroscopy and X-ray absorption nearedge spectroscopy (XANES) indicated the presence of Co<sup>II</sup> and Al<sup>III</sup> centers in DUT-5-CoH and DUT-5-Co after catalysis. The coordination environment of the cobalt center of DUT-5-Co before and after catalysis was established by extended



X-ray fine structure spectroscopy (EXAFS) and density functional theory. The kinetic and computational data suggest reversible carbonyl coordination to cobalt preceding the turnover-limiting step, which involves 1,2-insertion of the coordinated carbonyl into the cobalt-hydride bond. The unique coordination environment of the cobalt ion ligated by oxo-nodes within the porous framework and the rate independency on the pressure of  $H_2$  allow the deoxygenation reactions chemoselectively under ambient hydrogen pressure.

# ■ INTRODUCTION

Chemoselective deoxygenation of carbonyls and alcohols to the corresponding saturated compounds has drawn considerable attention for its diverse applications in fine-chemical synthesis and biofuel production. The conversion of abundant and renewable biomass-derived carbohydrates and lignocellulose to value-added chemicals and liquid fuels requires the cleavage of strong C–O bonds and the removal of most, or all, of the oxygen atoms in the reactants without cleaving C-C/C-H bonds.<sup>1-8</sup> Chemoselective deoxygenation methods also allow late-stage modification of the highly functionalized molecules and have been applied in the synthesis of many pharmaceuticals such as oxandrolone<sup>9</sup> and thromboxane receptor antagonist.<sup>10</sup> Classical methods for the deoxygenation of carbonyls and alcohols to the corresponding alkanes such as those based on the Barton–McCombie  $(R_3SnH)$ ,<sup>11</sup> borohydrides,<sup>12,13</sup> boranes,<sup>14,15</sup> Clemmensen (Zn/Hg, HCl),<sup>16</sup> HI/red-P,<sup>17</sup> and Wolff–Kishner–Huang  $(N_2H_4, KOH)$  reductions<sup>18–20</sup> are generally associated with rigorous reaction conditions, poor functional group tolerance, the utilization of stoichiometric amounts of reagents, and the generation of undesirable byproduct. To improve the atom economy and preclude hazardous reagents, transition-metal-catalyzed deoxygenation has been developed. Catalytic protocols for deoxygenation typically rely on the toxic and precious late transition metals and require a stoichiometric amount of reductants such as silane,<sup>21–26</sup> alcohol,<sup>27</sup> formic acid,<sup>28</sup> hydrazine,<sup>29</sup> or hydrogen.<sup>30–37</sup> Among all of the reductants, H<sub>2</sub> is the most atom-efficient and nontoxic and also produces H<sub>2</sub>O as the only byproduct. However, the catalytic deoxygenation reaction using H<sub>2</sub> (hydrodeoxygenation) is usually executed at high temperatures and pressures with the explosion risk. Therefore, the development of heterogeneous catalysts based on earth-abundant metals for hydrodeoxygenation under mild condition is challenging but highly attractive for economic reasons. Despite recent progress on supported earth-abundant metal nanoparticles-based catalysts for hydrodeoxygenation,<sup>38–42</sup> the requirement of high catalyst loading, high pressure of hydrogen, limited substrate scope, and ill-defined active sites limits their practical applicability and also complicates the investigation of the mechanism.

Metal-organic frameworks (MOFs) are an emerging class of porous and tunable molecular material to develop heterogeneous and well-defined earth-abundant metal catalysts.<sup>43-49</sup>

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#### Drawbacks of base metal catalysts:

• high metal loading • high pressure of H<sub>2</sub> • multi-sites and ill-defined catalysts



# (b) This work: Heterogeneous single-site cobalt catalyzed deoxygenation of carbonyls and alcohols

Figure 1. Hydrodeoxygenation of carbonyls and alcohols catalyzed by late transition metals<sup>21–27,29–31,33–36</sup> and base metals.<sup>28,37–41</sup>

MOFs, built from metal-oxo cluster-based secondary building units (SBUs) or nodes and organic bridging linkers, provide thermally and chemically robust solid platforms to afford siteisolated catalytically active species.<sup>50-54</sup> Unlike the traditional oxide supports such as silica, alumina, or other metal oxides, MOFs offer a unique oxide support at SBUs to prepare singlesite base-metal catalysts, benefitting from their reticular synthesis, tunable pores, and the highly disperse and uniform hydroxyl groups of its SBUs.55-64 Moreover, MOF-supported single-site catalysts provide both the leverages offered by homogeneous catalysts such as homogeneity of the active sites, reproducibility, and selectivity and those provided by heterogeneous counterparts such as excellent robustness and easy recycling of the catalysts.<sup>47,65-82</sup> Herein, we report an aluminum hydroxide SBUs in a robust MOF (DUT-5)supported single-site cobalt(II) hydride catalyst (DUT-5-CoH) for chemoselective deoxygenation of a range of aromatic and aliphatic ketones, aldehydes, and primary and secondary alcohols, including biomass-derived substrates under 1 bar of  $H_2$  (Figure 1).

## RESULTS AND DISCUSSION

**Synthesis and Characterization of DUT-5-CoH.** DUT-5-CoH was prepared by postsynthetic modification of aluminum hydroxide nodes of DUT-5. DUT-5 MOF, having a formula of [Al(OH)(bpdc)], is constructed from  $Al^{3+}$  cations that are octahedrally coordinated with  $\mu_2$ -hydroxide and 4,4'biphenyldicarboxylate (bpydc<sup>2-</sup>) bridging linkers to afford a three-dimensional (3D) porous framework with rhombic channels (Figure 2a).<sup>83,84</sup> DUT-5 was easily prepared by the solvothermal reaction of 4,4'-biphenyldicarboxylic acid (H<sub>2</sub>bpdc) and aluminum trichloride hexahydrate in dimethylformamide (DMF).<sup>83</sup> The deprotonation of  $\mu_2$ -OH of SBUs by *n*-BuLi followed by the salt metathesis reaction with  $CoCl_2$  in tetrahydrofuran (THF) afforded cobalt-functionalized DUT-5 (DUT-5-CoCl) as a blue solid. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis of the digested DUT-5-CoCl showed an Al/Co ratio of 3.45, corresponding to a formula of  $Al(O)(bpdc)(Li)_{0.71}(CoCl)_{0.29}$ . The crystallinity and structure of MOF remained intact after metalation as evidenced by the similar patterns of powder Xray diffraction (PXRD) between pristine DUT-5 and DUT-5-CoCl (Figure 2b). Thermogravimetric analysis revealed that DUT-5-CoCl is thermally robust up to 460 °C (Figure S3, Supporting information (SI)). DUT-5-CoCl has a BET surface area and pore size of 730 m<sup>2</sup>/g and 1.1 nm, respectively (Figure 2c). Spherical particles of DUT-5-CoCl with an average diameter of 0.9 nm were observed by transmission pubs.acs.org/IC



**Figure 2.** (a) Synthesis of DUT-5-CoH via postsynthetic metalation of DUT-5 MOF. (b) PXRD patterns of simulated DUT-5 (black), <sup>83</sup> freshly synthesized DUT-5 (blue), DUT-5-CoCl (red), DUT-5-CoH (green), and DUT-5-Co recovered after hydrodeoxygenation of 4-methoxy-acetophenone (magenta). (c) Brunauer–Emmett–Teller (BET) nitrogen sorption isotherms of DUT-5 and DUT-5-CoCl measured at 77 K. (d) EXAFS spectra and fits in R-space at the Co K-edge of DUT-5-CoCl(THF) with the magnitude and real component of the Fourier transformation shown as hollow triangles and hollow squares in blue color, respectively. The fitting range in R-space is 1.1-3.5 Å (within the gray lines). (e) Co K-edge values and for the Co Leck (green). (f) Co 2p X-ray photoelectron spectrum (XPS) of DUT-5-CoH. (g) EXAFS spectra and fits in R-space at the Co K-edge of DUT-5-CoH(THF) with the magnitude and real component of the Fourier transformation shown as hollow triangles and hollow squares in blue color, respectively. The future for the future for the Co K-edge of DUT-5-CoH (THF) with the magnitude and real component of the Fourier transformation shown as hollow triangles and hollow squares in blue color, respectively. The fitting range in R-space at the Co K-edge of DUT-5-CoH (THF) with the magnitude and real component of the Fourier transformation shown as hollow triangles and hollow squares in blue color, respectively. The fitting range in R-space is 1.1-3.5 Å (within the grey lines).

electron microscopy (Figure S2a, SI). The Co-coordination environment in DUT-5-CoCl was investigated by extended Xray absorption fine structure (EXAFS) at the Co K-edge, which was fitted with the density functional theory (DFT)-optimized structure of SBU-supported Co moiety within DUT-5-CoCl (Figure 2d). The DFT-optimized structure using the B3LYP method and a basis set of 6-311G(d,p) on Gaussian 09 software suits showed a distorted square pyramidal cobalt ion, which is coordinated with one  $\mu_2$ –O<sup>-</sup>, two neutral carboxylate oxygens, one chloride molecule, and one THF molecule to give the  $[(\mu_3-O)(\text{carboxylate-O})_2\text{CoCl}(\text{THF})]$  species.<sup>63</sup> The Co–  $(\mu_3$ -O) distance is 1.90 Å, while the Co-O(carboxylate) distances are 2.08 and 2.04 Å, respectively. Fitting the EXAFS feature of the Co centers in DUT-5-CoCl with this DFToptimized structure revealed nearly identical local coordination environment and bond lengths (Figure 2d). The similar energies of the pre-edge and K-edge peaks of DUT-5-CoCl and  $CoCl_2$  in X-ray absorption near-edge structure (XANES) indicate that the Co center in DUT-5-CoCl adopts the +2 oxidation state (Figure 2e).

The reaction of DUT-5-CoCl with 1.3 equiv of NaEt<sub>3</sub>BH with respect to cobalt in THF formed DUT-5-CoH via halide–hydride exchange. Crystallinity and the structural integrity of DUT-5 were maintained after the formation of cobalt-hydride at SBUs, as indicated by the similar PXRD patterns of DUT-5-CoH and DUT-5-CoCl (Figure 2b). Heating a mixture of DUT-5-CoH with H<sub>2</sub>O produced nearly 1 equiv of H<sub>2</sub> with respect to cobalt as analyzed by gas chromatography, suggesting the formation of cobalt-hydride after treating DUT-5-CoCl with NaEt<sub>3</sub>BH (Section 2.4, SI). XANES analysis showed a Co<sup>II</sup> oxidation state in DUT-5-CoH (Figure 2e). The assignment of the +2 oxidation state of cobalt

was further established by X-ray photoelectron spectroscopy (XPS), which displayed a  $2p_{3/2}$  peak at 781.6 eV and a  $2p_{1/2}$  peak at 797.8 eV (Figure 2f). Fitting of the EXAFS region of DUT-5-CoH at the Co K-edge with DFT-calculated ( $\mu_3$ -O)(O-carboxylate)<sub>2</sub>CoH(THF) structure model revealed the coordination of each Co<sup>II</sup> center to one  $\mu_3$ -O<sup>-</sup>, two neutral carboxylate oxygen atoms, one hydride, and one THF in a distorted square pyramidal geometry, similar to DUT-5-CoCl(THF) (Figure 2g). The calculated Co-( $\mu_3$ -O<sup>-</sup>) distance of 1.96 Å, Co-(carboxylate-O) distances of 2.01 and 1.99 Å, Co-(THF-O) distance of 2.17 Å, and Co-H distance of 1.51 Å are similar to those measured by EXAFS fitting (2.01, 2.04, 2.04, 2.21, and 1.45 Å, respectively). Importantly, no EXAFS feature corresponding to metallic Co nanoparticles was observed.

DUT-5-CoH-Catalyzed Hydrodeoxygenation of Carbonyl Compounds. DUT-5-CoH is an excellent catalyst for deoxygenation of ketones and related secondary alcohols using H<sub>2</sub> as the reducing agent. First, the reaction condition of hydrodeoxygenation of benzophenone was optimized by varying the temperature and pressure of H<sub>2</sub> (Table S1, SI). At a 0.4 mol % Co loading, DUT-5-Co-catalyzed deoxygenation of benzophenone at 60 °C under 4 bar H<sub>2</sub> in toluene for 22 h afforded an equal mixture of diphenylmethane and diphenylmethanol in 25% conversion as detected by gas chromatography-mass spectrometry (GC-MS). Upon increasing the temperature to 80 °C, diphenylmethane was obtained in quantitative yield. Interestingly, the conversion was found to be independent of the pressure of H<sub>2</sub>. In general, the DUT-5-Co-catalyzed deoxygenation of ketones proceeded well at 80 °C using toluene or *p*-xylene as a solvent under 1 bar of H<sub>2</sub>. Under these optimized conditions, the deoxygenation of aryl alkyl ketones such as acetophenone and 2-methylacetophenone with 0.4 mol % of cobalt loading gave 100% conversion within 24 h to ethylbenzene (2a) and 2-ethyltoluene (2b), respectively (Scheme 1). DUT-5-Co-catalyzed deoxygenation of carbonyl-groups had a wide range of substrate scopes, including aryl alkyl ketones, diaryl ketones, naphthone, heterocyclic ketones, and aliphatic ketones with excellent auxiliary functional group tolerance (Scheme 1, 2a-z2). The deoxygenation of substituted acetophenones bearing both electron-rich groups such as methyl (1b), methoxy (1c-e), amino (1f-h), and hydroxo (1i-j) and electron-withdrawing groups such as halo (1m-n), ester (11), and amide (1k) occurred selectively under 1 bar of H2. The reduction of aromatic rings was not detected in all cases. The hydrogenation of substituted benzophenones such as 2-methylbenzophenone (1q), 2-aminobenzophenone (1r), and 2,5diaminobenzophenone (1s) were deoxygenated to 1-benzyl-2methylbenzene (2q), 2-benzylaniline (2r), and 2-benzylbenzene-1,4-diamine (2s), respectively, in quantitative GC-yields. Pure methylene compounds (2q-s) were afforded by the simple removal of solid MOF and volatiles from the crude products.

The performance of DUT-5-Co catalyst was further evaluated on other aryl alkyl phenyl ketones such as isopropyl phenyl ketone (1t), cyclopropyl phenyl ketone (1u), benzyl phenyl ketone (1v), and 2-acetylnaphthalene (1w). At a 0.4 mol % Co loading, the products 2t-w were afforded in excellent yields using our standard protocol under 1 bar H<sub>2</sub>. Heterocyclic ketones such as 4-acetylpyridine (1x), 2acetylpyridine (1y), and 2-acetylthiophene (1z) were also deoxygenated without any reduction of the aromatic rings. Scheme 1. Hydrodeoxygenation of Ketones Catalyzed by DUT-5-CoH $^{a,b,c,d}$ 

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<sup>*a*</sup>Reaction conditions: DUT-5-CoH (0.4 mol % Co), 0.243 mmol of ketone, 1 bar  $H_2$ , 3.0 mL of *p*-xylene, 80 °C, 24 h. <sup>*b*</sup>Yields were determined by GC-MS using 4-*tert*-butyl-toluene as the internal standard, isolated yields within parentheses. <sup>*c*</sup>Reaction was carried out at 110 °C. <sup>*d*</sup>Substrate: 4-acetylbenzaldehyde.

However, the substrate bearing both keto and aldehyde groups such as 4-acetylbenzalhehyde (1z2) furnished 4-ethylbenzyl alcohol in 100% conversion at 80  $^{\circ}$ C, suggesting that the aldehyde group is intolerable under the reaction conditions.

Several experiments were performed to examine the heterogeneity of the MOF catalyst in the hydrodeoxygenation of ketones. The rate of deoxygenation of 4-methoxyacetophenone was unchanged upon addition of the metallic mercury to the reaction mixture, suggesting any leached metallic cobalt was not responsible for the catalysis (Figure S7, SI). Co nanoparticles, synthesized via reduction of CoCl<sub>2</sub> by NaEt<sub>3</sub>BH, were far less active and selective than DUT-5-Co, precluding the involvement of any in situ generated Co particles as the potential catalyst in the deoxygenation reactions (Figure S9,

SI). Furthermore, the progress of deoxygenation reaction ceased immediately after removing the solid MOF catalyst from the reaction mixture (Figure S6, SI). Importantly, no apparent loss of catalytic activity of DUT-5-Co was observed after its recycling and reuse for five consecutive runs in deoxygenation of 4-methoxyacetophenone (Figure 3a). During



Figure 3. (a) % GC yield of the products at several runs in the recycle and reuse experiment of DUT-5-Co (0.4 mol % Co) for hydrodeoxygenation of 4-methoxyacetophenone. (b) Plots of % GC yield of alcohol (red) and alkane (gray) after hydrodeoxygenation of benzophenone (A, B) and 2-acetylnapthalene (C, D), using DUT-5-Co (0.4 mol % Co, A and C) and MIL-53(Al)-Co (0.4 mol % Co, B and D) under similar reaction conditions.

the recycling experiment, the leaching of cobalt and aluminum from the MOF into the solution after the first run was 0.05 and 0.03%, respectively, and that was 0.26 and 0.08%, respectively, after the fourth run. The PXRD pattern of the recovered DUT-5-Co after run 6 was almost unchanged (Figure 2b), signifying the retention of the crystallinity of DUT-5-Co during the catalysis. We also compared the catalytic activity and selectivity of DUT-5-CoH with MIL-53(Al)-supported cobalt(II) hydride to investigate the effect of pore size on the deoxygenation reactions (Figure 3b).<sup>63</sup> Both DUT-5-CoH and MIL-53(Al)-CoH have similar framework topology and identical coordination environment of cobalt;<sup>63</sup> however, pore sizes of DUT-5-CoH are larger than those of MIL-53(Al)-CoH. DUT-5-CoH was more active and selective than MIL- 53(Al)-CoH in deoxygenation of relatively bulky and rigid substrates such as benzophenone and 2-acetylnaphthalene. At a 0.4 mol % Co loading, DUT-5-CoH-catalyzed deoxygenation of 2-acetylnaphthalene at 80 °C for 18 h afforded 2-ethylnaphthalene in 97% yield. In contrast, under identical reaction conditions, MIL-53(Al)-CoH gave only 1-(2-naphthyl)ethanol in 36% conversion (Figure 3b). The superior activity of DUT-5-CoH over MIL-53(Al)-CoH is likely due to the facile diffusion of the reactant and product molecules within its larger pores.

DUT-5-CoH-Catalyzed Deoxygenation of Aldehydes and Primary Alcohols by Hydrogen. DUT-5-CoH was also an active catalyst for the hydrodeoxygenation of aldehydes and primary alcohols under 1 bar  $H_2$  (Scheme 2). However, the deoxygenation of aldehydes requires a higher temperature at





<sup>*a*</sup>Reaction conditions: DUT-5-CoH (0.4 mol % Co), 0.243 mmol of ketone, 1 bar H<sub>2</sub>, 3.0 mL of *p*-xylene, 120 °C, 24 h. <sup>*b*</sup>Yields were determined by GC-MS using 4-*tert*-butyl-toluene as the internal standard, isolated yields within parentheses. <sup>*c*</sup>Reaction was carried out at 140 °C. <sup>*d*</sup>Substrate: furfural, reaction was carried out in methyl cyclohexane at 180 °C under 40 bar H<sub>2</sub> for 48 h.



**Figure 4.** (a) Time evaluation plot of DUT-5-Co-catalyzed deoxygenation of 4-methoxyacetophenone. (b) EXAFS spectra and fits in *R*-space at the Co K-edge of DUT-5-Co after deoxygenation of 4-methoxyacetophenone with the magnitude and real component of the Fourier transformation shown as hollow triangles and hollow squares in blue color, respectively. The fitting range in *R*-space is 1.1–3.5 Å (within the gray lines). (c) SEM image and SEM-EDX mapping of Al and Co in DUT-5-Co particles recovered after catalysis. (d) Plots of initial rates for hydrodeoxygenation of 4-methoxyacetophenone versus initial average concentrations of cobalt and 4-methoxyacetophenone. (e) Proposed catalytic cycle of hydrodeoxygenation of carbonyl compounds. (f) DFT-calculated energy profile diagram of DUT-5-Co-catalyzed deoxygenation of carbonyls using hydrogen. See the SI for computational details.

120 °C compared to that of ketones. At a 0.4 mol % of cobalt loading, DUT-5-CoH-catalyzed hydrodeoxygenation reaction of 4-methoxybenzaldehyde at 120 °C under 1 bar  $H_2$  for 24 h produced 4-methylanisole (4a) in quantitative yield.

Similarly, under the identical reaction conditions, substituted benzaldehydes bearing functional groups such as methoxy (3a-d), hydroxy (3e-g), amino (3i-j), amide (3k), and halo (3m-n) were deoxygenated chemoselectively to afford the corresponding methylarenes in excellent yields. Benzo[d][1,3]-dioxole-5-carbaldehyde (3h) and 4-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)benzaldehyde (**3o**) were transformed to 5methylbenzo[d][1,3]dioxole (**4h**) and 4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (**4o**) with 99 and 98% yields, respectively. The deoxygenation of heterocyclic aldehydes such as pyrrole-2-carboxaldehyde (**3p**), 2-pyridinecarboxaldehyde (**3q**), and indole-3-carbaldehyde (**3r**) also proceeded well at 120 °C under 1 bar H<sub>2</sub>. Ketoprofen was deoxygenated to the corresponding products (**4s**) in 67% yield keeping the carboxylic acid group intact. The hydrodeoxygenation of aliphatic substrates requires harsher reaction conditions. 1Octanol (3t), 1-undecanol (3u), and 3-phenylpropanal (3v) were converted to octane (4t), undecane (4u), and propylbenzene (4v), respectively, at 140 °C. Interestingly, at a 0.4 mol % Co loading, DUT-5-CoH was efficient to deoxygenate biomass-derived 5-(hydroxymethyl)furfural (3w), furfuryl alcohol (3x), and furfural (3y) to furnish the corresponding methylfurans in excellent yields. When the reaction with furfural was performed at 180 °C under 40 bar  $H_2$ , hydrogenation of arene also occurred simultaneously, and 2-methyltetrahydrofuran (4z) was obtained as the sole product, which is an important organic solvent and has potential application as a biofuel (Scheme 2).<sup>85,86</sup>

Mechanistic Investigation of DUT-5-CoH-Catalyzed Hydrodeoxygenation of Carbonyl Compounds. The reaction of DUT-5-CoH (0.4 mol % Co) and 4-methoxyacetophenone under 1 bar of H2 at 80 °C first produced 1-(4methoxyphenyl)ethanol without a detectable induction period. The time evaluation studies of the same reaction showed the formation of 1-(4-methoxyphenyl)ethanol as the major product in the first half-life, and no trace of 4-vinylanisole or any other side product was observed during the course of the reaction (Figure 4a). We thus infer that the deoxygenation reactions occur in two sequential pathways, where the carbonyls are first reduced to alcohols, and the subsequent deoxygenation of alcohols produces the corresponding methylene compounds. The XANES analysis of DUT-5-Co recovered after deoxygenation of 4-methoxyacetophenone suggests the existence of Co<sup>II</sup> species after catalysis (Figure 2e). EXAFS studies of the recovered DUT-5-Co were also conducted to identify the cobalt species as the catalyst resting state. The EXAFS at the Co K-edge was well fitted with the DFT-calculated coordination environment of a cobalthydroxide complex, indicating the formation of  $(\mu_3 - O^-)$ -(O<sub>carboxylate</sub>)<sub>2</sub>Co(OH) species after catalysis (Figure 4b). We observed a significant misfit of EXAFS data using the model of DUT-5-Co(OH) including 5% of cobalt nanoparticles, which suggests that cobalt nanoparticles were not formed during the catalysis. In addition, the PXRD of DUT-5-CoH and DUT-5-Co after catalysis displayed no characteristic reflection peaks at higher  $2\theta$  angles, ruling out the formation of Co nanoparticles upon reaction with NaEt<sub>3</sub>BH and during the catalysis (Figure 2b). Furthermore, scanning electron microscopy (SEM)energy-dispersive X-ray (EDX) mapping of DUT-5-Co recovered after catalysis indicated that Co and Al are uniformly dispersed throughout the MOF particle (Figure 4c). Therefore, we surmise that the node-supported Co<sup>II</sup> hydride in DUT-5-CoH was the active catalytic site for the hydrodeoxygenation of carbonyl compounds, and the proposed catalytic cycle is displayed in Figure 4e. We propose that the coordination of carbonyl to the cobalt center followed by 1,2-insertion of the carbonyl into cobalt-hydride bond generates cobalt-alkoxide intermediate, which then undergoes  $\sigma$ -bond metathesis with H<sub>2</sub> to give the alcohol (Cycle-1, Figure 4e). Subsequently, the coordination of this alcohol to the cobalt center of DUT-5-CoH followed by  $\sigma$ -bond metathesis between Co-H and C-O bond generates the deoxygenated product and the Cohydroxide intermediate (Cycle-2, Figure 4e). The subsequent  $\sigma$ -bond metathesis of Co-hydroxide and H<sub>2</sub> regenerates the cobalt-hydride catalyst with the production of water.

The reaction pathway of DUT-5-CoH-catalyzed deoxygenation of 4-methoxyacetophenone to 4-ethylanisole was further characterized by kinetic and DFT studies. Plots of ln[4methoxyacetophenone] versus time were linear up to two halflives (Figure S11b, SI), and this is consistent with the rate to be the first-order-dependent on substrate concentration. However, after two half-lives, the reaction rate decreased and deviated from the linearity, presumably due to the inhibition by the water and alcohols. To minimize the inhibition effect, we determined the empirical rate law by the methods of initial rates (Section 4.2, SI). The concentration of 4-methoxyacetophenone was calculated by GC-FID using 4-tert-butyl-toluene as the internal standard. As shown in Figure 4d, the initial rate increases linearly on increasing the substrate concentration at a lower range of substrate concentrations (0.03-0.13 M); however, it reaches maxima at higher substrate concentrations (>0.13 M). The saturation kinetics thus indicate reversible carbonyl coordination to cobalt preceding the rate-determining step. Besides, the initial rates have a first-order rate dependence on the concentration of cobalt (Figure 4d) but are independent on H<sub>2</sub> pressure ranging from 2 to 20 bar (Figure S12, SI). The kinetic data of deoxygenation of 4methoxyacetophenone indicate a cobalt ion and a carbonyl molecule participating in the rate-determining step.

We performed DFT calculations to further understand the mechanism of the catalytic hydrogenolysis of carbonyls (Figure 4f). The coordination of 4-methoxyacetophenone to cobalt forms a distorted square pyramidal cobalt-intermediate (INT-1), which has a 6.8 kcal/mol higher energy than DUT-5-CoH. Then, 1,2-insertion of the coordinated carbonyl into Co-H bond in the transition state-1 (TS-1), which requires an activation energy of 3.5 kcal/mol, gives cobalt-alkoxide intermediate (INT-2). In the next step, INT-2 is transformed to 1-(4-methoxyphenyl)ethanol and  $\bar{\rm D}{\rm UT}$ -5-CoH via  $\sigma$ -bond metathesis of Co-O bond with H<sub>2</sub> in TS-2 requiring an activation free energy of 10.9 kcal (Figure 4f). The regenerated DUT-5-CoH further catalyzes the deoxygenation of 1-(4methoxyphenyl)ethanol to produce 4-ethylanisole and water as shown in Cycle-2 in Figure 4e. The coordination of 1-(4methoxyphenyl)ethanol to cobalt of DUT-5-CoH gives INT-3, which undergoes  $\sigma$ -bond metathesis of Co–H bond and C–O bond of the coordinated alcohol in TS-3 to afford cobalthydroxide intermediate (INT-4). The transformation of INT-3 to INT-4 has an energy barrier of 2.8 kcal/mol. In addition, the formation of INT-4 and 4-ethylanisole from INT-3 is exergonic by 29.9 kcal/mol. Finally,  $\sigma$ -bond metathesis between the Co-O bond of INT-4 and dihydrogen releases water and regenerates DUT-5-CoH. The DFT-calculated energy profile diagram identifies the conversion of cobalthydride of INT-1 to the corresponding cobalt-alkoxide intermediate (INT-2) via TS-1 as the rate-determining step of the catalytic cycle. The calculated structure of TS-1 reveals a four-member cyclic transition state involving the insertion of the carbonyl group into the Co-H. The nature of the plot of initial rates versus substrate concentrations is also consistent with our theoretical studies, which displayed a first-order rate dependency at lower substrate concentrations followed by rate independency at a higher substrate concentration suggesting the reversible carbonyl coordination to cobalt to form INT-1 preceding the rate-determining step (Figure 4e,f).

The DFT studies indicate that the coordination environment of cobalt at the SBUs within the pores of MOF lowers the activation energy of the binding and the interaction with small  $H_2$  molecule (TS-2 and TS-4, Figure 4) compared to those with relatively much bulkier carbonyl substrates resulting in a zeroth-order reaction with respect to the pressure of  $H_2$ . The independency of initial rate on  $H_2$  pressure allows all of the deoxygenation reactions to occur under 1 bar of H<sub>2</sub>. Furthermore, NBO population analysis identifies electron-rich hydride and  $\mu_3$ -oxo sites with charges of -0.535 and -1.40, respectively, in DUT-5-CoH (Table S5, SI). We thus assume that the reactive and highly polar Co hydride facilitates the insertion of the unsaturated carbonyl bonds, leading to excellent catalytic performance. Interestingly, our DFT calculation suggests that the neutral O(carboxylate) ligands at SBUs weakly coordinate to the cobalt ion to stabilize the active cobalt-hydride species within the MOF. Furthermore, the labile Co-O(carboxylate) bonds also dissociate in the sterically congested turnover-limiting step (TS-1) to create vacant coordination sites at the cobalt center for substrate binding and activation. We surmise that the high catalytic efficiency of DUT-5-Co under mild reaction conditions is originated due to the presence of single-site and reactive Co-H bonds, the unique coordination environment of cobalt(II) ion at SBUs ligated by both anion and neutral oxo ligands, and the uniform distribution of cobalt-hydride species through the large MOF channels.

# **CONCLUSIONS**

In conclusion, a mild and cost-effective method for the deoxygenation of a wide range of aromatic and aliphatic aldehydes, ketones, and alcohols using an easily affordable MOF-supported cobalt catalyst is described. This cobalt catalyst was synthesized by metalation of aluminum hydroxide nodes of the DUT-5 with CoCl<sub>2</sub> followed by the reaction with NaEt<sub>3</sub>BH. Our synthetic protocol displayed excellent tolerance for a wide range of functional groups such as aryl, amines, amides, esters, and hydroxyl, and also utilized cheap and atomeconomical reductant hydrogen. The mechanism of the catalytic hydrodeoxygenation was investigated in detail by spectroscopic, kinetic, and computational studies. The unique coordination environment of cobalt ion ligated by both neutral and monoanionic oxo ligands of SBUs within the porous framework and the rate independency on the pressure of H<sub>2</sub> bring the chemoselectively of deoxygenation reactions under 1 bar of H<sub>2</sub>. This work highlights the development of novel catalytic technologies based on earth-abundant metal-functionalized MOFs for efficient hydrodeoxygenation of C-O bonds in biomass and organic molecules for sustainable synthesis of chemical feedstocks and biofuels.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01008.

Synthesis and characterization of DUT-5-MOF and DUT-5-Co; experimental details for catalytic reactions; details of kinetics, EXAFS, and GC analysis; and DFT calculations (PDF)

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#### Notes

The authors declare no competing financial interest.

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