

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201800729 Angew. Chem. 10.1002/ange.201800729

Link to VoR: http://dx.doi.org/10.1002/anie.201800729 http://dx.doi.org/10.1002/ange.201800729

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Selective hydrogenation of CO₂ into ethanol over cobalt catalysts

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Abstract: Hydrogenation of CO₂ into valuable chemicals is in great demand but still challengeable. Here we report the selective hydrogenation of CO₂ into ethanol over non-noble cobalt catalysts (CoAlO_x), presenting a significant advancement for the conversion of CO₂ into ethanol as a major product. By adjusting the Co-CoO_x composition of the catalysts under different pre-reduction temperatures, the efficiency of CO₂ hydrogenation to ethanol was well optimized over the catalyst reduced at 600 °C, giving ethanol selectivity of 92.1% at 140 °C with the ethanol time yield at 0.444 mmol g⁻¹ h⁻¹. Operando FT-IR spectroscopy reveals that the high selectivity of ethanol over the CoAlO_x catalyst is ascribed to the formation of acetate from formate with the insertion of *CH_x, the key intermediate to produce ethanol from CO₂ hydrogenation.

Ethanol is a very useful chemical in both industry and our daily life, which has been widely used as a clean fuel additive, solvent, and disinfectant.^[1] The conventional route of ethanol production relies on the fermentation of cellulosic feedstock, which competes for food with the human beings.^[1c] Developing new routes of ethanol production with industrial potentiality is of great importance, and a scope of successes have been achieved from syngas.^[1a,b] Particularly, an attractive route is the employment of CO₂ as feedstock since its significant advantages including easy availability and renewability, which is also attractive for eliminating the greenhouse gas by converting CO₂ into valuable chemicals.^[2-4] However, the CO₂-to-ethanol transformation is difficult owing to the chemical inertness of CO₂. Effective cleavage of the C=O

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bond and selective formation of desired chemicals are still challenging.

A scope of effective catalysts have been developed for the hydrogenation of CO2, [2-4] typically the ceria-titania decorated with Au,^[3a] Cu,^[3b] industrial Cu/ZnO/Al₂O₃,^[2b,c] Ni-Ga,^[3d] Zn-Zr,^[4a] Mn- $\text{Co},^{[4b]}$ Fe-Co $^{[4c]}$ catalysts. However, these catalysts provide methanol as major product. In the past few years, the homogeneous catalysts assembled with air-sensitive organic ligand emerged to be selective catalysts for the production of C2+ products from CO2 hydrogenation,^[5] but these homogeneous catalysts are difficult to be regenerated or even separated from the reaction system. Heterogeneous catalysts are favorable for the CO₂ hydrogenation and can easily overcome the issues in catalyst regeneration. Therefore, supported noble metal catalysts (Pd and Pt) have attracted much attention in CO₂ hydrogenation due to their extraordinary ability in C-C coupling, an important step of $C_{\geq 2}$ molecule production.^[6] But the co-existence of mixed C_{2+} alcohol products leads to limited ethanol selectivity. The replacement of the scarce and expensive noble metals with cheap and abundant first-row transition metals, such as cobalt, which is well known as efficient catalyst for the C-C coupling-based reactions (e.g. Fischer-Tropsch synthesis),^[7] would enhance the sustainability of the CO₂ hydrogenation. In regard to the ethanol synthesis from hydrogenation of CO₂, the challenges of potentially practical and sustainable routes rely on employing abundant metal catalysts and forming ethanol at high selectivity, which is in great demand but extremely difficult to achieve.

Herein, we reported the selective hydrogenation of CO₂ to ethanol with abundant cobalt catalysts. Key to this success is the employment of cobalt catalysts derived from Co-Al layered double hydroxide (LDH), followed by calcination and reduction to form alumina supported cobalt particles (CoAlO_x). By optimizing the reduction temperature to adjust the Co-CoO_x phases on the CoAlO_x catalysts, the efficiency of CO₂ hydrogenation to ethanol was well optimized with the catalyst reduced at 600 °C, showing ethanol selectivity of 92.1% at 140 °C with the ethanol time-yield at 0.444 mmol g⁻¹ h⁻¹. This result is even comparable with the Pt catalysts,^[6a] outperforming all abundant metal catalysts in CO₂ hydrogenation to ethanol reported previously. Mechanism study demonstrates that the transformation undergoes CO₂ adsorption and activation, formate intermediates formation, insertion to acetate, and hydrogenation to produce ethanol. More importantly, the catalyst is stable and exhibits constant performances in continuous recycle tests.

The cobalt catalysts for CO₂ hydrogenation were derived from the Co-Al layered double hydroxide, which was synthesized by a co-precipitation assisted with urea, followed by calcination to Co-Al mixed oxides. After reduction in hydrogen at different temperatures from 300 to 650 °C, the alumina supported cobalt catalysts were obtained, which are denoted as CoAlO_x-T(T is the reduction temperature).

Figure 1 shows the catalytic data of various catalysts in the hydrogenation of CO_2 at 140 and 200 °C. The pure alumina without cobalt species is inactive for the reaction. Interestingly,

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the CoAlO_x catalysts are always active, giving ethanol as a major product, but methanol, n-propanol and n-butanol are also detectable. The time-yield and selectivity of ethanol over CoAlO_x catalysts are sensitive to the reduction temperature performed on the catalysts, and the best performance was achieved over CoAlO_x-600 by optimizing the solvents, catalyst amount, and cobalt content (Figures S1-S6, Table S1), giving ethanol selectivity of 92.1% at 140 °C, where the time-yield of ethanol can reach as high as 0.444 mmol g_{cat}-1 h-1. Further increasing the reaction temperature to 200 °C gave enhanced alcohol productivity of 1.003 mmol g_{cat} -1 h-1 with ethanol selectivity of 88.9% (Figure S7). In this case, the ethanol productivity (0.892 mmol g_{cat}^{-1} h⁻¹) is even higher than the time yield of all the C₂₊ alcohols over Pt-based catalysts,^[6a] which are regarded to be superior catalysts for CO₂-to-high alcohol transformation. More importantly, CO, methane, and higher hydrocarbons, which are general gaseous products in CO₂ hydrogenation, were undetectable after the reaction over CoAlOx-600. Lower reduction temperature led to a significant decrease in activity and ethanol selectivity. When the catalyst was reduced at 300 °C, the total time-yield of alcohol products was only 0.269 mmol g_{cat}⁻¹ h⁻¹ over CoAlO_x-300 catalyst with ethanol selectivity of 64.3% at 140 $^{\circ}$ C. In contrast, the commercial Co₃O₄ reduced at 600 °C displayed poor selectivity to ethanol of 25.8%. The Cu/ZnO/Al₂O₃ catalyst, which has been widely utilized for CO₂ hydrogenation,^[2b,c] gave only methanol as the product at 140 °C and CO existed at 200 °C with undetectable ethanol. The alumina supported Fe- and Nicatalysts exhibited methanol as major product with a slight amount of ethanol under the equivalent reaction conditions (Figure S8, Tables S2 and S3). All these data confirm the extraordinary catalytic performances of CoAlO_x catalysts for the CO₂-to-ethanol transformation (Figure S9).



Figure 1. Data showing the catalytic performances of various catalyts in CO_2 hydrogeantion. Reaction conditions: 20 mg of catalyst, 2 mL of H₂O solvent, initial pressure 4.0 MPa (H₂/CO₂ = 3:1), 15 h, reaction temperature at (a) 140 and (b) 200 °C. The yields and selectivities were based on the moles of carbon.

Figure 2a shows the XRD patterns of various samples, where the reduction at high temperatures (e.g. 500-650 °C) led to the subsequent formation of CoO and Co as dominant phases (Figure

absorption near-edge S10). X-rav structure (XANES) spectroscopy was carried out to investigate the coordination and the oxidation state of Co on the CoAlO_x samples. Figure 2b shows that the Co K-edge feature changed from Co₃O₄ to CoO by reduction at 400 °C. After the reduction 600 °C, the metallic Co appeared with the co-existence of oxide. This transformation was further evidenced by the extended X-ray absorption fine structure (EXAFS) results (Figure 2c). With the increase of reduction temperature from 300 °C to 400 °C, the intensity of Co-O decreased, the Co-Co (CoO_x) transformed from peaks at 2.86 and 3.37 Å to a single peak at 3.00 Å (phase shift corrected), suggesting the formation of CoO as a dominant phase. The edge features of metallic Co (Co-Co with R = 2.51 Å) obviously appeared after reduction at 600 °C with co-existence of CoO (Co-O with R = 1.97 Å and Co-Co with R = 2.98 Å), which might explain the higher activity of CoAlOx-600 than CoAlOx-300 and CoAlOx-400 because the activation of hydrogen normally requires metallic sites. In the end, the Co-Co coordination in metallic Co (coordination number at 3.6) became dominant on CoAlOx-600 with a slight signal of Co-Co coordination in CoO (coordination number at 1.0, Table S4). We speculate that the presence of metallic Co is necessary for the efficient hydrogenation of CO₂ to ethanol, and the co-existence of Co and CoO_x phases might be favorable, because the reduction at higher temperature for CoAlOx-650 with more metallic Co species and slight amount of CoO_x (Figure 2a) showed enhanced methanol yields and decreased ethanol yields compared to CoAlO_x-600 (Figure S11).



Figure 2. Structure characterization of CoAlO_x catalysts. (a) XRD patterns of CoAl-LDH, Co-Al oxides and CoAlO_x catalysts reduced at different temperatures. (b) Co K-edge XANES. (c) EXAFS of various CoAlO_x samples.

Figure 3a shows scanning electron microscopy (SEM) image of CoAlO_x-600. Although the layered structure was destroyed by calcination (see the XRD patterns), the plate-like morphology still remained. Transmission electron microscopy (TEM) provides a direct observation of the CoAlO_x-600 sample, showing highly dispersed Co particles with a mean size of 4.6 nm on the amorphous Al₂O₃ support. The Co nanoparticles were well identified on Al₂O₃ support by using high-angle annular dark fieldscanning transmission electron microscopy (HAADF-STEM) image (Figure 3c), where the Co species display brighter contrast than Al₂O₃. The Co and Al distribution was further confirmed by using EDX elemental maps in Figures 3d-f (Figure S12), obviously showing the dispersion of Co nanoparticles on Al₂O₃ support which are in good agreement with the STEM image.

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The surface geometry of the CoAlO_x catalysts was further studied by HR-TEM characterization. For CoAlO_x-600 catalyst, the faceting of Co particles changed along the line where the boundary terminates at the surface, assigning to the co-existing phases of metallic Co and CoO (Figure 3h), as confirmed by a Fast Fourier transform (FFT) analysis (Figure 3i). The electron energy loss spectrum (EELS) of CoAlOx-600 gives the approximate ratio 4.2 of Co L3 and L2 edges, locating between metallic Co and CoO. It indicates the Co valence locates between 0 and +2, suggesting the CoO and Co are the dominating phases of CoAlO_x-600.^[8] Notably, the used CoAlO_x-600 catalyst after five runs in CO₂ hydrogenation still exhibits similar phases to the fresh catalyst (Figure S13), demonstrating its good stability. The CoAlO_x reduced at different temperatures gives distinguishable phases. The CoAlOx-300 has pure Co3O4, and metallic Co is almost undetectable. Increasing the reduction temperatures at 400-650 °C led to the subsequent formation of CoO and metallic Co (Figures S14-S18), which is proved by the HR-TEM images.



Figure 3. Electronic microscopy characterization of CoAlO_x-600. (a) SEM image. (b) TEM image (insert: size distribution of Co NPs). (c-f) HAADF-STEM image (c), EDX elemental maps (d: CoAlO_x-600; e: Al, f: Co). (g-i) HRTEM images (g and h), The corresponding FFT image of Co NPs (i) in (h). (j) EELS result. The pink cycles highlighted the cobalt particles.

To determine how the Co phases influence the catalytic performances, we investigated the adsorption of CO₂ on the catalysts by *in-situ* FTIR. As shown in Figure 4a, the biggest difference among the CO₂ adsorption on CoAlO_x samples is that CoAlO_x-400 and CoAlO_x-500 have weak signals at 1396 and 1434 cm⁻¹, while CoAlO_x-600 and CoAlO_x-650 give a single and sharp peak at 1434 cm⁻¹ with strong intensity, demonstrating that a large amount of CO₂ (CO₃²⁻) was asymmetrically adsorbed on CoAlO_x-600 and CoAlO_x-650 samples (Figure S19).

To investigate the reaction intermediates, the *operando* FTIR was carried out to understand the interaction between CO₂ and hydrogen on the cobalt catalysts (Figure 4b), where the bands at 1038, 1362, 1471, 1584, and 2895 cm⁻¹ appeared. The bands at 1038 and 1362 cm⁻¹ correspond to the ethoxy species, and the bands at 1471, 1584, and 2895 cm⁻¹ can be assigned to the acetate species.^[9-11] All these data confirm the formation of C₂-oxygen of ethoxy and acetate species on CoAlO_x-600 from CO₂ hydrogenation, which are regarded as important intermediates for ethanol production. Similar bands assigned to C₂-oxygen intermediates were also observed in the *in-situ* IR spectra of CO₂ hydrogenation over CoAlO_x-500 and CoAlO_x-650 catalysts. It seems that the Co-CoO_x phases are important to the formation of C₂-oxygen intermediate, and CoAlO_x-400 without metallic Co phases gives very weak bands of C₂-oxygen (Figures 4b and S20),

which might explain the relatively lower ethanol selectivity/productivity over CoAlO_x-400 catalyst than those over CoAlO_x-500, CoAlO_x-600 and CoAlO_x-650. On the contrary, the Cu/ZnO/Al₂O₃ catalyst gave the bands of various C₁-oxygen intermediates with completely undetectable C₂-species (Figures S21 and S22),^[9] which might explain the sole production of methanol on Cu/ZnO/Al₂O₃ catalyst.



Figure 4. *In situ* FTIR and ¹H NMR spectroscopy investigation. (a and b) *In situ* FTIR spectra of (A) CoAIO_x-400, (B) CoAIO_x-500, (C) CoAIO_x-600, and (D) CoAIO_x-650 at 350 °C with different feed gases of (a) CO₂ and (b) CO₂ and H₂ with molar ratio at 1/3. (c and d) ¹H NMR spectrum (c) and ¹H COSY NMR spectrum (d) of the mixture in the reactor during the reaction. (e) *In situ* FTIR spectra of CoAIO_x-600 in a continuous CO₂ flow with pulsed H₂.

The formation of C₂-species was further confirmed by the ¹H MAS NMR spectrum of the reaction mixture (Figure 4c), which gives signals at 0.72 and1.35 ppm assigned to *CH₃ group and *CH₂ species bonded to the oxygen on the CoAlO_x-600 catalyst surface (*C₁-oxygen), respectively. ¹H homonuclear chemical shift correlation (COSY) spectrum (Figure 4d) showed cross contours at (1.35, 0.72) and (0.72, 1.35), indicating that the aforementioned *CH₃ and *C₁-oxygen groups on the catalyst surface are interrelated. These two signals should come from the -C-C bond structure with characteristics of the two signals. These results suggest that the *CH₃ prefers to couple with *C₁-oxygen species to form C₂-oxygen species, rather than deep hydrogenation for the formation of methane product, which might explain the undetectable methane in the gaseous products.

In order to gain more detailed information on the reaction intermediates, we performed the *operando* FTIR spectra of CoAlO_x-600 in a continuous CO₂ flow with pulsed hydrogen, where the hydrogen are insufficient to decelerate the transformation. As shown in Figure 4e, the CO₂⁵⁻, CO₃²⁻, and HCO₃⁵⁻ species (1229, 1430, 1649 cm⁻¹) appeared at the beginning of the reaction due to the primary adsorption and activation of CO₂ (Figure S23).^[11] After pulsing slight amount of hydrogen, the above signals are remarkably decreased, giving new bands at 1373, 1594 and 2904 cm⁻¹. The band at 2904 cm⁻¹ confirmed the presence unsaturated C-H species (*CH_x), and the bands at 1373 and 1594 cm⁻¹ are assigned to symmetric and asymmetric OCO stretches of formate (HCOO⁻) species.^[12]

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Generally, the formate species is stable and difficult to be hydrogenized,^[3b] thus hinders methanol formation over the CoAlO_x-600 catalyst. Interestingly, further introduction of hydrogen into the catalyst caused the decrease of formate bands, but giving the new bands at 1521-1584 cm⁻¹, which are assigned to the asymmetric OCO stretches in the acetate species.^[13] The formation of acetate is further confirmed by another new band at 2896 cm⁻¹ assigned to saturated C-H. Meanwhile, the bands of unsaturated C-H species (*CH_x, 2904 cm⁻¹) and formate (1373 cm⁻¹) were significantly reduced (Figure 4e), giving the new bands associated with C2-oxygen species. These results suggest that the $*CH_x$ is indeed transformed into C₂-oxygen species via the insertion,^[2d,12] which might hinder further hydrogenation for the formation of methane. Compared to formate, the C=O bond in acetate group is weakened, benefiting the further hydrogenation to form ethoxy species (1360 cm⁻¹) when more hydrogen was introduced.^[14] All these data confirmed that the ethanol formation follows the steps of CO₂ adsorption and activation, formate intermediates formation. transformation to acetate. and hydrogenation to produce ethanol. According to these data, the high ethanol selectivity over CoAlOx-600 might be attributed to the high reducibility of the surface oxides, which enhanced the hydrogenation ability to produce *CH_x intermediate to transform formate to acetate, an important intermediate for ethanol production. On the other hand, poorly reduced oxide surface, such as CoAlOx-400, leads to relatively lower activity and selectivity to ethanol but enhanced methanol selectivity, which is likely due to the weak hydrogenation activity to form acetate intermediate (Figure 4b).

In summary, we reported an efficient strategy for ethanol synthesis from the hydrogenation of CO_2 by using cobalt catalysts (CoAIO_x) obtained from the Co-Al layered double hydroxides. The best catalytic performances was achieved over CoAIO_x-600, which exhibits good activity and extraordinary selectivity as well as high stability for the selective hydrogenation of CO_2 to ethanol. The improved performances over CoAIO_x-600 is likely due to the optimized surface oxides with co-existence of Co-CoO phases, which benefit the production of *CH_x for converting formate into acetate *via* insertion, an important intermediate for ethanol production. This work might not only expand the territory of CO_2 hydrogenation for selective production of ethanol, but also open an avenue for developing non-noble metal catalysts for CO_2 conversion.

Acknowledgements

This work is supported by National Key Research and Development Program of China (2017YFC0211101) and National

Natural Science Foundation of China (21720102001, 91634201 and 91645105), Natural Science Foundation of Zhejiang Province (LR18B030002), and the Jilin Province/Jilin University co-Construction Project-Funds for New Materials (SXGJSF2017-3, Branch-2/No.440050316A36). We acknowledge beamtime at Shanghai Synchrotron Radiation Facility (SSRF, beamline BL14W1).

Keywords: CO₂ hydrogenation · cobalt catalyst · ethanol

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Transformation of greenhouse gases CO₂ into ethanol: A persuasive CO₂-toethanol transformation over designed cobalt catalysts gives superior ethanol selectivity, which is reasonably ascribed to the formation of acetate from formate with the insertion of $*CH_x$, the key intermediate to produce ethanol from CO₂ hydrogenation.



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