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Highly Selective Hydrogenation of CO₂ to Ethanol via Designed Bifunctional $Ir_1-In_2O_3$ Single-Atom Catalyst

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ABSTRACT: Recently, CO₂ hydrogenation for the controlled growth of the carbon chain to produce high-value C₂ or C₂₊ products has attracted great interest, where achieving high selectivity for a specific product remains a challenge, especially for ethanol. Herein, we have designed a bifunctional $Ir_1-In_2O_3$ single-atom catalyst, integrating two active catalytic centers by anchoring the monatomic Ir onto the In_2O_3 carrier. This $Ir_1-In_2O_3$ single-atom catalyst is efficient for the hydrogenation of CO₂ in liquid, yielding a high selectivity for ethanol (>99%) with an excellent initial turnover frequency (481 h⁻¹). Characterization shows that the isolated Ir atom couples with the adjacent oxygen vacancy forming a Lewis acid-base pair, which activates the CO₂ and forms the intermediate species of carbonyl (CO*) adsorbed on the Ir atom. Coupling this CO* with the methoxide adsorbed on the In_2O_3 forms a C-C bond. The strategy of this effective bifunctional single-atom catalyst by synergistically utilizing the distinct catalytic roles of the single-atom site and the substrates provides a new avenue in catalyst design for complex catalysis.

It is paramount to reduce the dependence on fossil energy and to control CO_2 emissions by developing renewable energies.^{1,2} One of the most attractive strategies is to close the carbon cycle by producing "liquid sunlight" by transforming CO_2 into liquid fuel.³ Thus, much attention is paid to the hydrogenation of CO₂ into safe and transportable liquid hydrocarbons, including alcohols and gasoline.^{4,5} Among them, ethanol is one of the most desirable products due to its impressive energy density and existing engine technology.⁶ However, the direct synthesis of ethanol from CO₂ is still challenging due to the high energy barrier of C–C coupling.⁷ The synthesis of ethanol from CO₂ has been realized using Rh-, Fe-, or Co-based catalysts via an indirect Fischer-Tropsch synthesis (FTS). Although C-C coupling can be greatly promoted in FTS, the degree of C-C coupling is difficult to control. The produced alcohols follow the Anderson–Schulz–Flory (ASF) distribution with a typical ethanol fraction of \sim 35%.

In an effort to improve ethanol selectivity, recent research has focused on the design and modification of novel catalysts for CO_2 hydrogenation. Regulating active sites was the most effective method to govern the carbon chain growth with controlled alcohol distribution. For example, by modifying Cuor Co-based catalysts with ordered and isolated active sites, the ethanol selectivity was improved.^{13–17} For this catalyst, the separation of the catalytic site was essential for attaining control over the carbon chain growth. Here, we propose a new catalyst design strategy based on a single-atom catalyst (SAC) with uniformly distributed atomic active sites¹⁸ to maximize the ethanol selectivity. More importantly, SAC also serves as a bridge between homogeneous and heterogeneous catalysis. Our previous research suggests that the catalytic process that normally occurs with the homogeneous catalyst can be well realized using supported SACs.^{19,20}

Here, we designed a bifunctional SAC based on the synergy of atomic Ir with In_2O_3 for converting of CO_2 to ethanol. In_2O_3 is an effective catalyst for hydrogenation of CO_2 to produce methanol,²¹ while the Ir-based mononuclear complex can catalyze methanol carbonylation.^{22,23} We achieved excellent ethanol selectivity of 99.7% with the highest initial turnover frequency (TOF) of 481 h⁻¹, outperforming the precious metal catalysts. Theoretical calculation and infrared spectra revealed that a Lewis acid–base pair was formed between the monatomic Ir and the adjacent oxygen vacancy (O_v) on In_2O_3 forming two distinct catalytic centers, which reduces CO_2 to active intermediates and then facilitates the C–C coupling to form ethanol.

The Ir₁–In₂O₃ SAC was synthesized through a modified wet-chemical method. In₂O₃ was partially reduced with hydrogen to generate O_v before Ir impregnation.²¹ O_v served as the anchoring site for single atoms and trapped IrCl₆²⁻ with great affinity(Figure 1a).²⁴ The Ir loading in the Ir₁–In₂O₃ SAC was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES, Table S1). High angle darkfield scanning transmission electron microscope images confirmed the isolated single-atom structure of Ir (HAADF-STEM, Figures 1b and S1), where no nanoparticles were observed (Figure S2). Furthermore, the extended X-ray absorption fine structure (EXAFS) of the Ir L_{III} -edge of the $k^2 \chi$ (k) data showed the Ir–O coordination number to be 4.8



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Figure 1. (a) Schematic illustration of the fabrication procedures of $Ir_1-In_2O_3$. (b) HAADF-STEM image of $Ir_1-In_2O_3$. Inset scale bar, 5 nm. (c) Ir L_{III7} -edge EXAFS spectra in r-space with different Ir loadings (without phase correction). (d) Wavelet transform of the k^2 -weighted EXAFS spectrum of the $Ir_1-In_2O_3$. (e) The fitted XPS spectra of Ir 4*f* with diverse Ir loadings.

(Table S2) without Ir–Ir contribution²⁵ (Figure 1c). The wavelet transformed plot of $Ir_1-In_2O_3$ (Figure 1d) demonstrates the existence of Ir single atoms. X-ray photoelectron spectroscopy (XPS) (Figure 1e) revealed the binding energies (BE) of 65.2 and 62.1 eV for Ir $f_{5/2}$ and $f_{7/2}$, corresponding to the higher oxidation state of $Ir^{\delta+26}$.

The $Ir_1 - In_2O_3$ SAC was then used for CO_2 hydrogenation reactions in aqueous solution. Both gaseous and liquid products were analyzed after the reaction, where only methanol and ethanol were detected. Where pure In₂O₃ only produced methanol, the Ir₁-In₂O₃ SAC preferentially yielded ethanol with a selectivity of 99.7% and a $\mathrm{TOF}_{\mathrm{Ir}}$ value up to 481 h^{-1} (Figures 2a and b). This TOF was comparable with the best literature results reported under similar conditions (Table S3). Since the catalytic kinetics are dependent on the reaction temperature, the dependency of ethanol production on time and temperature was also investigated. As the temperature increased from 180 to 240 °C, the yields of both ethanol and methanol increased monotonically (Figure 2c). However, the methanol yield increased at a higher rate, such that the selectivity of ethanol decreased to 92.2% at 240 °C. Hence, a lower temperature is more favorable to ethanol production. As for reaction time, we found that the initial ethanol yield was relatively low (0.016 mmol g^{-1} h⁻¹) but increased to 0.99 mmol g^{-1} h⁻¹ after 5 h (Figure 2d). Meanwhile, the methanol yield remained constant at 0.012 mmol g⁻¹ h⁻¹, resulting in an increase of ethanol selectivity from 51.6% to 99.7%. The results suggested that the ethanol selectivity depended on the relative production of methanol, which in turn indicated indirectly that methanol could be an important intermediate for ethanol synthesis. The research of different solvents, metals, and

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Figure 2. (a) Selectivity of ROHs (methanol and ethanol) and achieved the yield of ethanol and (b) comparisons of the TOF_{Ir} values over different Ir loadings on In₂O₃ during CO₂ hydrogenation at 200 °C for 5 h. ROH yields and ethanol selectivity over Ir₁–In₂O₃: effect of temperature (c) and reaction time (d) in 3.0 mL of H₂O, initial pressure 6.0 MPa (H₂ /CO₂ = 5:1), catalyst 20 mg.

supports claimed that the selection of components $(Ir-In_2O_3)$ in the polar solvent was crucial (Tables S4 and S5).

The excellent catalytic performance of $Ir_1-In_2O_3$ SAC was closely related to its structure. Electrostatic potentials of In_2O_3 and $Ir_1-In_2O_3$ were calculated to investigate the catalytic mechanism (Figure 3a and b). The presence of monatomic Ir



Figure 3. Electrostatic potential figures of In_2O_3 (a) and $Ir_1-In_2O_3$ catalyst surface (b). Free energy diagram for CO_2 dissociation over the In_2O_3 and $Ir_1-In_2O_3$ catalyst (c).

created a negative potential, while the oxygen vacancy (O_v) remained positively charged on the defective In_2O_3 basal surface. As such, a local Lewis acid–base pair was formed between the monatomic Ir and the adjacent O_v . DFT calculations demonstrated that CO_2 was more favorably adsorbed onto $Ir_1-In_2O_3$ than onto In_2O_3 (Figure 3c). Chemisorbed CO_2 formed CO_2^* (asterisk (*) represents the surface-adsorbed species), where the C atom was directly bound to the Ir atom and one of the O atoms was bound to the adjacent O_v . This indicated a synergistic effect toward CO_2 activation. The distinct adsorption geometry presented by the $Ir_1-In_2O_3$ catalyst enabled a decrease in the energy barrier for CO_2^* dissociation to CO^* from 0.77 eV on pure In_2O_3 to 0.48 eV. The resulting Ir^{δ^+} – CO^* intermediate was thought to play a critical role in ethanol production.²⁷

The CO₂ transformation was also verified by the *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Figures 4a,b and S3). A key intermediate of CO (2076 cm⁻¹) appeared on Ir_1 - In_2O_3 after exposing CO₂ at 200



Figure 4. DRIFTS spectra of pure In_2O_3 (a) and $Ir_1-In_2O_3$ catalyst (b) after exposure to CO_2 at 200 °C. In situ FTIR spectra (c) of CO_2 hydrogenation with $Ir_1-In_2O_3$ catalyst bubbled in aqueous solution. $Ir-In_2O_3$ samples with different Ir loadings (d) after exposure to CO_2 at 200 °C.

°C, confirmed the $Ir^{\delta+}$ -CO* formation.²⁸⁻³⁰ The peak intensities attributed to carbonate (1309, 1365, and 1496 cm⁻¹) and bicarbonate (1450 and 1630 cm⁻¹) moieties^{31,32} were notably higher on $Ir_1-In_2O_3$ than those on pure In_2O_3 , implying that the effect of the Lewis acid-base pair on CO₂ activation was promoted. The adsorption of CO* was deemed strong since no significant reduction of CO peak intensity in Ar flush experiments (Figure S4). Meanwhile, the formation of another important intermediate CH₃O* (2856, 2960, and 2994 cm⁻¹)^{33,34} was observed during hydrogenation with in situ Fourier transform infrared spectroscopy (FTIR, Figure 4c). These peaks have rarely been observed using pure In_2O_3 based methanol catalysts, suggesting that the Ir single atoms also help to stabilize the methoxide on the O_v of $Ir_1-In_2O_3$. Combined with the ¹³CH₃OH isotope experiment (Figure S5), we concluded that the stable intermediates of Ir^{δ_+} -CO* and $CH_3O^*-O_y$ were the pivotal species for C-C coupling.³⁵ The proposed reaction path is shown in Scheme S1.

The excellent catalytic performance of the $Ir_1-In_2O_3$ SAC was the colocalization of atomically dispersed Ir and O_v in the carrier phase. The importance of the atomic dispersion of Ir was examined by preparing $Ir-In_2O_3$ catalysts with increased Ir loading and then testing them under identical conditions. The ethanol selectivity was suppressed significantly from 85.3% to 5.7%, as the Ir content increased from 0.2 wt % to 1.0 wt % (Figure 2a). The TOF also decreased accordingly (Figure 2b).

TEM and scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) images revealed the growth of Ir from small clusters (0.5 wt %, Figures S6-S8) to aggregated nanoparticles of 1-2 nm in size (1.0 wt %, Figure S9). The

above structural features were also supported by X-ray diffraction (XRD) patterns (Figure S10). The Ir L_{III} edge EXAFS spectra revealed the presence of Ir-Ir metallic bond with increasing intensity as the Ir loading augmented (Figures 1c and S11a; and Table S2). XPS spectra (Ir 4f, Figure 1e) showed that the peak intensities associated with metallic Ir⁰ enhanced with increasing Ir loading,³⁶ accompanied by the redshift in In 3*d* BE (Figure S11b and Table S6). The soft Xray absorption spectra (XAS) showed a decrease in peak intensity at the In *M*-edge and O *K*-edge as the Ir loading augmented (Figure S12).³⁷ Therefore, the increase of Ir also caused a reduction of In₂O₃. The excessive reduction of In₂O₃ at higher Ir contents was also confirmed in the temperatureprogrammed reduction (H₂-TPR, Figure S13 and Table S7). With the increase of Ir^0 , the In_2O_3 reduction peak shifted from 242 (In_2O_3) to 170 °C $(1.0 \text{ wt } \% \text{ Ir}-In_2O_3)$. The reduced In_2O_3 became less active^{21,38} toward the formation of methoxide with decreased ethanol selectivity. Besides, Ir1- $\rm In_2O_3$ showed a gradual decrease of TOF to a value of 186 $\rm h^{-1}$ after the fourth catalytic cycle (Table S8), also due to the reduction of In_2O_3 (Figure S14).

CO₂ activation was also affected by the increase in nonmonoatomic Ir loading. CO₂ DRIFTS showed that the amount of adsorbed CO₂ species significantly decreased as the Ir content increased (Figures 4d and S15). The formation of Ir⁰– CO was evidenced with a peak at a lower wavenumber of 2040 cm⁻¹ compared to Ir^{δ +}–CO.³⁰ Hence, the C–O bond strength was weaker on Ir⁰ than on Ir^{δ +} due to more electron transfer from Ir⁰ to CO 2 π antibonding orbital,³⁹ while the Ir⁰–C bond became stronger. This meant that the alkylation activity was lowered while the cleavage of the C–O bond became easier. The larger size of Ir^0 particles could also enrich the surface H concentration, resulting in a direct reduction of C_1 species forming methanol, while the C–C coupling activity decreased. Our results confirmed that the over-reduction of In_2O_3 would alter the coordination of critical intermediate components. Hence, the SAC design of the monatomic Ir on In_2O_3 was optimized for the selective hydrogenation of CO₂ to ethanol.

In conclusion, an $Ir_1-In_2O_3$ single-atom catalyst for CO_2 hydrogenation to ethanol was presented. Thanks to the bifunctional nature of the $Ir_1-In_2O_3$, composed of partially reduced In_2O_3 and a Lewis acid-base pair between the single-atom Ir and adjacent oxygen vacancy (O_v) , it not only promotes the adsorption and activation CO_2 into CO^* but also provides great opportunities for C-C coupling between $CH_3O^*-O_v$ and $Ir^{\delta+}-CO^*$. As a result, CO_2 was hydrogenated into ethanol with a selectivity up to 99.7% at an initial TOF up to 481 h⁻¹. Our study presents a new, green, and promising catalyst for the conversion of CO_2 into a versatile energy source; introduces the rational design of bifunctional single-atom catalysts for simplifying complex reaction processes, and expands the applications of single-atom catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08607.

Experimental procedures, details on the synthesis of Ir/ In_2O_3 catalysts, and additional characterizations of the Ir/ In_2O_3 catalysts (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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