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InNi$_3$C$_{0.5}$ catalyst is highly active, selective, and stable for the RWGS reaction.

InNi$_3$C$_{0.5}$(111) surface is gifted with dual active sites (3Ni-In and 3Ni-C).

CO$_2$ is dissociated into CO* (preferentially desorbed) on 3Ni-C and O* on 3Ni-In.

InNi$_3$C$_{0.5}$ is also promising for application in carbonyl-to-hydroxyl processes.

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Nano-Intermetallic InNi$_3$C$_{0.5}$ Compound Discovered as a Superior Catalyst for CO$_2$ Reutilization

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SUMMARY

CO$_2$ circular economy is urgently calling for the effective large-scale CO$_2$ reutilization technologies. The reverse water-gas shift (RWGS) reaction is the most techno-economically viable candidate for dealing with massive-volume CO$_2$ via downstream mature Fischer-Tropsch and methanol syntheses, but the desired groundbreaking catalyst represents a grand challenge. Here, we report the discovery of a nano-intermetallic InNi$_3$C$_{0.5}$ catalyst, for example, being particularly active, selective, and stable for the RWGS reaction. The InNi$_3$C$_{0.5}$(111) surface is dominantly exposed and gifted with dual active sites (3Ni-In and 3Ni-C), which in synergy efficiently dissociate CO$_2$ into CO$^*$ (on 3Ni-C) and O$^*$ (on 3Ni-In). O$^*$ can facilely react with 3Ni-C-offered H$^*$ to form H$_2$O. Interestingly, CO$^*$ is mainly desorbed at and above 400°C, whereas alternatively hydrogenated to CH$_3$OH highly selectively below 300°C. Moreover, this nano-intermetallic can also fully hydrogenate CO-derived dimethyl oxalate to ethylene glycol (commodity chemical) with high selectivity (above 96%) and favorable stability.

INTRODUCTION

Concerns about the vital global warming and ocean acidification problems caused by CO$_2$ excessive emission (Karl and Trenberth, 2003; Orr et al., 2005) have triggered extensive researches on its large-scale reutilization via effective, economical, and sustainable technologies for a CO$_2$ circular economy (Aresta et al., 2014; Porosoff et al., 2016). However, industrialized CO$_2$ reutilization is just limited to the synthesis of urea and polycarbonate (occupying only 0.5% of CO$_2$ emissions), whereas enzymatic and electro-/photo-chemical strategies are hampered by their low CO$_2$-conversion efficiency (Wang et al., 2008; Kondratenko et al., 2013). To achieve the large-scale CO$_2$ reutilization, CO$_2$ hydrogenation with renewable-energy-generated H$_2$ to CO by the reverse water-gas shift (RWGS) reaction is the most techno-economically viable candidate (Porosoff et al., 2016; Kondratenko et al., 2013; Xu and Moulijn, 1996; Porosoff and Chen, 2013; Zhang et al., 2017), thanks not only to its high efficiency, enabling to deal with vast amounts of CO$_2$, but also to the great versatility of syngas (CO + H$_2$, product gas of RWGS reaction) to produce commodity chemicals and fuels (occupying 40% CO$_2$ emissions [Zhang et al., 2017] via mature Fischer-Tropsch and methanol (CH$_3$OH) syntheses [Porosoff et al., 2016; Kondrat et al., 2016]).

The RWGS reaction is an equilibrium-limited endothermic reaction (required enthalpy of 41.17 kJ mol$^{-1}$). According to Le Châtelier’s principle, high-temperature (about 400–800°C) thermodynamically favors high CO$_2$ conversion and high CO selectivity, but the undesired methanation also proceeds under the preferred RWGS conditions (Chen et al., 2001; Wu et al., 2015; Gonçalves et al., 2017; Yang et al., 2017). Therefore, a techno-economically available catalyst with outstanding CO$_2$-to-syngas performance is the prerequisite for the large-scale RWGS implementation. To date, homogeneous complexes and heterogeneous solids catalysts have been extensively explored. The homogeneous catalysts show satisfactory activity and selectivity (Federselel et al., 2010), but their difficult recovery from the reaction mixture makes them unattractive. The heterogeneous catalysts are more competitive in terms of ready catalyst-product separation and continuous processes. They mainly include the nanoparticules of precious metals (e.g., Au, Ag, Pt) (Porosoff et al., 2016; Yang et al., 2017) and non-precious metals (e.g., Cu, Ni) (Zhang et al., 2017; Chen et al., 2001; Wu et al., 2015; Gonçalves et al., 2017) dispersed on supports (e.g., SiO$_2$, Al$_2$O$_3$, CeO$_2$, MoC$_x$) (Porosoff et al., 2016; Zhang et al., 2017; Chen et al., 2001; Wu et al., 2015; Gonçalves et al., 2017; Yang et al., 2017). Despite the excellent RWGS activity, the precious-metal catalysts suffer from their limited natural abundance. Cu and Ni catalysts are intensively studied but are not promising owing to either serious sintering (Cu) (Zhang et al., 2017; Chen et al., 2001) or high methanation activity (Ni) (Wu et al., 2015; Gonçalves et al., 2017).
Given the chemical inertness of CO$_2$ molecule (Xu and Moulijn, 1996), the heart of RWGS is to exquisitely design and tailor a groundbreaking catalytic material with both high efficiency and low cost, but this represents a grand challenge within the CO$_2$-conversion field.

Against all odds, the tantalizing progresses in nano-intermetallic catalysis (Stamenkovic et al., 2007; Studt et al., 2014) open an opportunity for designing and tailoring qualified RWGS catalysts because nano-intermetallic has fascinating prospects in catalysis field, with their tunable components and ratios, variable constructions, and reconfigurable electronic structures, distinctly different from their single metals (Stamenkovic et al., 2007; Armbruster et al., 2012; Ji et al., 2010). Particularly, their precise atomic ordering structure can provide rational predictions of the effects of geometry and electronic structure on their catalytic properties for required reactions (Wang et al., 2013; Nicholson et al., 2014; Qin et al., 2018). One of the recent pertinent examples is the discovery of a Ni$_5$Ga$_3$ nano-intermetallic, which strikingly shows that the Ni, originally active for CO$_2$ methanation, turns itself suddenly into a qualified CO$_2$-to-CH$_3$OH catalyst after Ga alloying (Studt et al., 2014), because this intermetallic offers the unique Ga-rich sites for CH$_3$OH formation. Encouraged by these big achievements toward nano-intermetallic catalysis, we believe that the nano-intermetallic can pave a road to the rational engineering of more intelligent catalysts gifted with flexibly arranged atomic structures and tailor-made catalytic properties for the RWGS reaction as well as other reactions for CO$_2$ reutilization.

Here, we present a nano-intermetallic InNi$_3$C$_{0.5}$ catalyst that is particularly active, selective, and stable for the RWGS reaction under extremely wide reaction conditions. Such nano-intermetallic is fabricated via carburizing the In-Ni nano-intermetallic in the real RWGS stream and is gifted with dual active sites (i.e., 3Ni-In and 3Ni-C) on the InNi$_3$C$_{0.5}$(111) surface. The dual sites act in synergy to facilely dissociate CO$_2^*$ (adsorbed on 3Ni-In sites) into CO* (on 3Ni-C sites) and O* (on 3Ni-In sites), and the O* can favorably react with 3Ni-C offered H* to form H$_2$O. Most notably, the CO* is mainly desorbed into gas phase at and above 400°C but can be highly selectively hydrogenated to form CH$_3$OH below 300°C with a promising CO$_2$-to-CH$_3$OH capacity. Furthermore, this nano-intermetallic can fully hydrogenate dimethyl oxalate (obtainable from oxidative coupling of CO (Fenton and Steinward, 1974), product of the RWGS) to ethylene glycol (a commodity chemical) with high selectivity (above 96%) and favorable stability.

RESULTS

Discovery of InNi$_3$C$_{0.5}$ and Its Application for RWGS Reaction

To exquisitely tailor a groundbreaking RWGS catalyst, the elaborate choice of appropriate elements oriented by this reaction should be initially conducted but poses a great challenge because the relevant elements for this reaction traverse most of the periodic table. The first metal that mostly attracts attention is Ni, because Ni-based catalysts are typically used for the RWGS reaction despite CH$_4$ formation (Wu et al., 2015; Gonçalves et al., 2017). Moreover, In is another attractive element, because In-based catalysts are burgeoning in CO$_2$ conversion (Ye et al., 2012; Park et al., 2017; Larrazábal et al., 2016), and, for example, the intermetallic AgIn catalyst is highly efficient for electrochemical reduction of CO$_2$ to CO (Park et al., 2017; Larrazábal et al., 2016). We thus surmise that In-Ni intermetallic could reconstruct geometric-electronic structures of Ni, which might be feasible to switch Ni catalysis in CO$_2$ reduction from CH$_4$ formation to CO formation.

A series of pure intermetallics of InNi, InNi$_2$, and InNi$_3$ were successfully synthesized (Figure 1A) and then were evaluated for the RWGS reaction. Comparison with the conventional Cu-based catalysts (Zhang et al., 2017; Chen et al., 2001) reveals that the intermetallic In-Ni catalysts deliver exciting intrinsic RWGS performances, especially for InNi$_3$ with a high CO formation rate of 1.96 mmol g$_{\text{cat}}^{-1}$ min$^{-1}$ and a considerably low CH$_4$ selectivity (Figure S1). It is very intriguing to find that after reaction the InNi, InNi$_2$, and InNi$_3$ phases are in situ changed in association with a new phase formation of InNi$_3$C$_{0.5}$ (Figure 1B, identified in following section). Consistently, the InNi$_3$C$_{0.5}$ formation is thermodynamically favorable with large ordering energy (such as 2.72 eV for InNi$_3$ carburization with CO, Figure S2), which also portends that the InNi$_3$C$_{0.5}$ is stable under the RWGS conditions. Notably, only InNi$_3$ could be fully transformed into pure InNi$_3$C$_{0.5}$ owing to the identical stoichiometric In:Ni ratios of 3:1 and offers the highest RWGS performance, indicating that InNi$_3$C$_{0.5}$ should be responsible for the RWGS reaction.

The above-mentioned results and analyses make us confident that the InNi$_3$C$_{0.5}$ intermetallic is a superior RWGS catalyst. To make it a practical catalyst, the thin-felt Al$_2$O$_3$/Al-fiber substrate consisting of 10 vol%
60-μm Al2O3/Al-fiber and 90 vol% voidage (Wang et al., 2016) was used to support 9 wt% InNi3C0.5. This strategy permits the engineering of InNi3C0.5 nano-intermetallic at “nano-meso-macro” triple-scale levels of both porosity and structure in one step (Figures 2A–2C, S3A, and S3B), thereby making the catalyst development and reaction engineering (for enhanced heat/mass transfer) go hand in hand (Wang et al., 2016; Li et al., 2015). The InNi3C0.5/Al2O3/Al-fiber catalyst was tested for the RWGS reaction in a tubular fixed-bed reactor. As expected, this catalyst always achieves high CO2 conversions very close to the thermodynamic equilibrium values with above 97% CO selectivity under the wide reaction conditions (Figures 2D–2F). For example, a 53% CO2 conversion is obtainable, quite close to the equilibrium value of 54%, at 540°C and a gas hourly space velocity (GHSV) of 54,000 mL gcat⁻¹ h⁻¹. This catalyst delivers a very high intrinsic activity with a turnover frequency (TOF) of 11.0 CO per active site per second at 540°C (see detailed TOF calculation in Supplemental Information), almost one to two orders of magnitude higher than that seen with most platinum/oxide and non-noble-metal catalysts (Table S1). Furthermore, a kinetic study was carried out over the InNi3C0.5/Al2O3/Al-fiber catalyst, and the apparent activation energy was calculated with the result as shown in Figure S3D. InNi3C0.5/Al2O3/Al-fiber provided a much lower Ea (60 kJ/mol) than Cu/ZnO-based catalysts (112 kJ/mol, Schumann et al., 2015), further indicating that this catalyst has a high intrinsic activity. Also encouraging is the exclusive CO selectivity (above 98%) with pressure increasing from 1.0 to 4.0 MPa at 540°C (Figure 2F), despite the fact that CH4 formation is much favorable at high pressure over the conventional Ni-based catalysts (Wu et al., 2015; Gonçalves et al., 2017; Li et al., 2015).

Stability is a significant consideration for catalysts in practical applications. Our InNi3C0.5/Al2O3/Al-fiber catalyst is very stable with 52%–53% CO2 conversion and 97%–99% CO selectivity throughout the entire 150 h testing at a GHSV of 54,000 mL gcat⁻¹ h⁻¹ and 540°C (Figure 2G). Even at a high GHSV of 300,000 mL gcat⁻¹ h⁻¹ and 600°C, the InNi3C0.5/Al2O3/Al-fiber catalyst also shows a high stability with no deactivation sign throughout 65 h testing (Figure 2H). In comparison, the Cu/β-Mo2C catalyst maintains 85% of its initial activity after 40 h reaction and the Cu/ZnO/Al2O3 catalyst loses more than 60% of its initial activity within 15 h reaction under the identical reaction conditions (Zhang et al., 2017). It is not surprising that the InNi3C0.5 crystalline phase, surface morphology, and structure of the used catalysts are preserved unchanged (Figures S3E–S3H), consistent with the excellent activity/selectivity maintenance in Figures 2G and 2H. To the best of our knowledge, the InNi3C0.5 intermetallic has never been used before for any application in catalysis, and herein we discover its superior RWGS performance—including CO2 conversion, CO selectivity, and especially high-temperature stability—over the reported state-of-the-art catalysts (Table S1).

Structure Identification

To definitely identify the crystal structure and composition of the as-formed carbide-intermetallic from In-Ni intermetallics, such pure carbide-intermetallic was synthesized via fully carburizing InNi3, and its X-ray diffraction (XRD) pattern completely coincides with the one of InNi3C0.5 that has an anti-perovskite-type structure (Joint Committee on Powder Diffraction File No. 28-0468; Figure 3A and Table S2).
Moreover, the In:Ni:C molar ratio of the as-synthesized InNi₃C₀.₅ was determined to be 1:2.99:0.49 (see elemental analyses in Supplemental Information), quite close to its stoichiometric ratio.

Figure 3B shows its structural model containing eight InNi₃ units. For each unit, eight In atoms occupy the eight corners and six Ni atoms occupy the six face centers; four C atoms randomly disperse in these eight body centers, but with the most stable configuration in a regular tetrahedron (Figure S4). The Wulff equilibrium shape of the InNi₃C₀.₅ nanocrystal was further optimized, and its optimum shape exposes fourteen surfaces.

Figure 2. Structural and Morphological Features of the InNi₃C₀.₅/Al₂O₃/Al-fiber Catalyst and Its RWGS Performance

(A) Optical photograph (top) and scanning electron microscopy (SEM) image (bottom) of the fresh catalyst.
(B) High-magnitude SEM image of the fresh catalyst.
(C) TEM images of the fresh catalyst (inset: lattice fringes with distance of 0.218 nm corresponding to the InNi₃C₀.₅(111) surface).
(D–F) CO₂ conversion, product selectivity, and CO-formation rate as a function of (D) reaction temperature (at a GHSV of 21,600 mL g⁻¹ h⁻¹ and 4.0 MPa), (E) GHSV (at 540 °C and 4.0 MPa), and (F) reaction pressure (at a GHSV of 54,000 mL g⁻¹ h⁻¹ and 540 °C) for a feed gas of H₂/CO₂/N₂ with molar ratio of 66/22/12.
(G and H) Time on stream under different reaction conditions and comparison (H) with the reported literature data over the commercial Cu/ZnO/Al₂O₃ (Zhang et al., 2017) and Cu/β-Mo₂C (Zhang et al., 2017) catalysts.
consisting of eight hexagons and six squares (Figure 3C). The InNi3C0.5(111) is the most stable surface of the hexagonal shapes with the lowest surface free energy (Table S3). Interestingly, high-resolution transmission electron microscopy (TEM) also displays an approximate hexagonal morphology of the real synthetic InNi3C0.5 nanoparticles (Figures 3D, 3E, and S5), and the lattice spacing of 0.218 nm is assignable to the InNi3C0.5(111) surface.

**Theoretical Calculations Study**

In the last decade, significant advances have been achieved in the atomistic-theoretical calculations, enabling us to computationally construct molecular and crystalline structures and to reveal the reaction pathways on the catalyst surface at atomic-molecular level (Nicholson et al., 2014; Qin et al., 2018; Studt et al., 2014; Mao et al., 2017). Therefore, the RWGS reaction mechanism on InNi3C0.5 is first investigated by the density functional theory (DFT) calculations. We selected the most stable InNi3C0.5(111) as the ideal surface and established the dual active sites (h1: Hollow(3Ni-In); h2: Hollow(3Ni-C); Figure 4A) from nine kinds of possible active sites (see detailed results in Table S4). As shown in Figure 4B, the CO2 molecule is chemically adsorbed via a bending configuration to form CO2* on h1 site, and the H2 molecule spontaneously dissociates into H* that can be adsorbed on both h1 and h2 sites. Electron density distribution for the dual active sites is richer than the others, which makes them more nucleophilic and more favorable for CO2 activation (Figure S6). Therefore, the CO2* facilely dissociates into CO* adsorbed on h2 site and O* adsorbed on h1 site with moderate exothermicity (namely, reaction energy $E_a$ = 0.38 eV) and a low activation barrier ($E_a$, 0.32 eV) but with higher $E_a$ of CO2* hydrogenation to formate (HCOO*, 0.42 eV) and to carboxyl (COOH*, 0.75 eV, Figure S7 and Table S5). Clearly, the CO2* dissociation to CO* and O* (i.e., redox pathway) is preferred over the formate and carboxyl pathways on the InNi3C0.5(111) surface. Furthermore, the formed O* on h1 site preferably reacts with H* on the neighboring h2 site to produce an OH* group ($E_a$, 0.73 eV), and subsequently, two OH* groups on the dual sites are easily transformed into H2O* ($E_a$, 0.25 eV) that is finally desorbed into the gas phase ($E_a$, 0.35 eV). The dual active

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**Figure 3. Structure and Morphology of the InNi3C0.5 Nano-Intermetallic**

(A) XRD pattern of the as-synthesized InNi3C0.5 nano-intermetallic.

(B) Ball-and-stick perspective of polyhedral InNi3C0.5 (a 2 x 2 x 2 super cell) with cubic (Fm3m) anti-perovskite-type structure (green octahedron, C-Ni6).

(C) Optimum Wulff equilibrium shape of InNi3C0.5 crystal.

(D) TEM image of the as-synthesized InNi3C0.5 nano-intermetallic, showing its uniform hexagonal shape (marked by yellow dashed lines).

(E) High-resolution TEM image of a typical InNi3C0.5 nanoparticle with hexagonal shape and a lattice spacing of 0.218 nm corresponding to the InNi3C0.5(111) surface.
sites provide much lower $E_a$ than the sole h1 sites for the above-mentioned steps (see detailed results in Table S5), probably the consequences of appropriate adsorption of reaction intermediates in terms of their adsorption strength (Table S4) and the distance between them (the dual active sites have shorter

Figure 4. Dual Active Sites and Reaction Pathways for CO$_2$ Hydrogenation on the InNi$_3$C$_0.5$(111) Surface
(A) Side (left) and top (middle) views of the InNi$_3$C$_0.5$(111) surface, and detailed structure (right) of the dual active sites of "3Ni-In" (i.e., Hollow I by three Ni atoms and one In atom) and "3Ni-C" (i.e., Hollow II by three Ni atoms and one C atom).
(B and C) Energy profiles on the InNi$_3$C$_0.5$(111) surface for (B) the most favorable pathways to RWGS reaction and for (C) the competitive pathways for CO$_2$ hydrogenation to CO (green), CH$_3$OH (blue), and CH$_4$ (black), where the black, red, and white balls represent the C, O, and H atoms in the reactive species, respectively.
adjacent h1-h2 distance of 3.106 Å than the sole h1 sites with an adjacent h1-h1 distance of 5.345 Å, Figure 4A). In contrast, CO2* dissociation on Cu(111) becomes endothermic ($E_r$, +1.06 eV, thermodynamically unfavorable) and is kinetically unfavorable ($E_a$ of 1.55 eV versus 0.32 eV on InNi3C0.5(111), Figures 4B, S8, and S9).

The formed CO* either undergoes further hydrogenation to CH4 and/or CH3OH or desorbs into the gas phase. Figure 4C shows that CO* desorption overcomes a slightly higher $E_a$ of 1.36 eV at 0 K than the formation of CH4 (CH3*-to-CH4*, 1.27 eV) and CH3OH (CO*-to-HCO*, 1.05 eV), clearly exhibiting a possibility of CH3OH formation (see detailed results and discussion in Figures S10 and S11). It should be noted, however, that CO* desorption is thermodynamically more favorable at elevated temperatures (Figures S12 and S13) owing to the significant entropy contributions (Graciani et al., 2014), and therefore CO* is preferentially desorbed into gas phase rather than hydrogenated into CH3OH at our real RWGS temperature of 420°C – 600°C (see experimental results in Figures 2D–2F).

**Infrared Spectroscopy Study**

To verify the RWGS reaction pathway on InNi3C0.5 from experimental perspective, the in situ Fourier transform infrared (FTIR) spectroscopy analysis was carried out on pure InNi3C0.5 in a continuous H2/CO2/N2 (molar ratio of 66/22/12) flow at ambient pressure. As shown in Figure 5A, the linear adsorbed CO* species are formed from CO2 dissociation even at 50°C, evidenced by infrared (IR) bands (Martin et al., 2016) at 2132, 2107, 2094, 2077, and 2055 cm$^{-1}$. Along with the increase in the temperature, the IR band intensity of linear adsorbed CO* becomes slightly stronger from 50°C to 175°C, remains almost unchanged from 200°C to 250°C, and then diminishes until disappearance at 325°C. In addition, two new bands at 1942 and 1824 cm$^{-1}$ assignable to the bridge-absorbed CO* species (Dou et al., 2017) are observed at 100°C while becoming stronger and stronger along with the temperature. Plentiful gaseous CO starts to be detected only at 300°C, and its formation is favored with the temperature. Neither CH4 (at 3013 cm$^{-1}$)
nor formate and carboxyl species (at 1281 and 1360–1600 cm$^{-1}$) are detectable in the whole temperature range studied, coinciding with the DFT-suggested preferable formation of CO over CH$_4$, formate, and carboxyl. It should be also noticed that no adsorbed CO$_2$ species are detectable; a possible explanation is that the CO$_2$ adsorption-dissociation is too fast to be monitored by IR, also coinciding with the DFT-indicated very low $E_a$ of only 0.32 eV for CO$_2$* dissociation. These IR spectra undoubtedly validate the DFT results: CO$_2$ can be efficiently converted to CO via redox pathway rather than formate and carboxyl ones.

Moreover, DFT calculations on InNi$_3$C$_{0.5}$(111) surface predict the possibility of CH$_3$OH formation (Figures 4C and S10 and Table S5). CO* is first hydrogenated into HCO* ($E_a$, 1.05 eV), which is easily hydrogenated into CH$_2$O* ($E_a$, 0.32 eV); CH$_2$O* can be continuously hydrogenated into CH$_3$OH* (E$_a$, 0.65 eV) or CH$_3$O* (E$_a$, 0.60 eV); however, CH$_2$OH* is more favorably hydrogenated into CH$_3$OH* (E$_a$, 0.88 eV) over CH$_3$O* to CH$_2$OH* (E$_a$, 1.71 eV). Therefore, we infer that CH$_3$O* should be detectable by IR owing to its high accumulation and that CH$_3$OH can be formed through the CO*-to-HCO*-to-CH$_2$O*-to-CH$_2$OH*-to-CH$_3$OH* pathway (see detailed results and discussion in Figure S10). Indeed, CH$_3$O* with IR band at 1033 cm$^{-1}$ are detectable at 200–325°C (Figure 5B), whereas CH$_3$OH is detected by the on-line mass spectrometry (MS) at 220–310°C accompanied by gaseous CO formation above 300°C (Figure 5C). Notably, the absence of CH$_2$O* and CH$_2$OH* in situ IR spectra is probably a consequence of the low residence time of these species on the surface under atmospheric conditions (Graciani et al., 2014). These IR and MS spectra consistently display that CO* is hydrogenated into CH$_3$OH highly selectively below 300°C, whereas it is dominantly desorbed into gas phase above 300°C.

### Extended Application for CO$_2$-to-CH$_3$OH and Carbonyl-to-Hydroxyl Transformations

The above-mentioned DFT and FTIR results also make us confident that the InNi$_3$C$_{0.5}$ nano-intermetallic is a potential catalyst for the CO$_2$ hydrogenation to CH$_3$OH, which becomes more and more competing in recent years. With reaction temperature reduced from 400°C–600°C (for the RWGS reaction) to 300°C and below, the InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber indeed turns itself suddenly into a CO$_2$-to-CH$_3$OH catalyst, being capable of converting 1%–8% CO$_2$ into CH$_3$OH with 60%–98% selectivity (corresponding to the CH$_3$OH space time yield of 70–330 gMeOH kgcat$^{-1}$ h$^{-1}$) at 200°C–300°C (Table S6). The preferable CH$_3$OH formation rather than CO formation below 300°C is attributed to the fact that low temperatures thermodynamically favor further hydrogenation of CO* to CH$_3$OH* (Figures S12 and S13). These results exhibit an interesting temperature-dependent selectivity switching for CO$_2$ hydrogenation.

Moreover, in the light that CO$_2$ molecule has the carbonyl property and InNi$_3$C$_{0.5}$ intermetallic can efficiently activate CO$_2$ molecule, we wonder whether this catalyst is favorable for other carbonyl-compounds transformation, such as the hydrogenation of aldehydes/ketones/esters to corresponding alcohols. To avoid the adverse influence of acid groups on the surface of Al$_2$O$_3$, we directly supported the InNi$_3$C$_{0.5}$ nano-intermetallic onto a thin-sheet Ni-foam substrate with 110 pores per inch (Figure S14, see detailed preparation in Supplemental Information). Indeed, the InNi$_3$C$_{0.5}$/Ni-foam catalyst presents the satisfying activity and high product selectivity (Tables 1 and S7), providing the general and efficient ability to activate the C=O bond for

| Substrate | Target Product   | T (°C) | P (MPa) | WHSV (h$^{-1}$) | Conv. (%) | Sel. (%) |
|-----------|------------------|--------|---------|-----------------|-----------|----------|
| DMO       | EG               | 210    | 2.5     | 0.44            | 100/100$^b$ | 96.0/96.1$^b$ |
| Acetone   | Isopropanol      | 150    | 0.1     | 6.0             | 65.3      | >99      |
| Furfural  | Furfuryl alcohol | 180    | 0.5     | 0.7             | 98.3      | 91.0     |
| Cyclohexanone | Cyclohexanol     | 170    | 0.1     | 6.0             | 62.6      | >99      |
| Butanone  | Butanol          | 120    | 0.1     | 5.0             | 57.3      | 98.1     |
| Salicylaldehyde | Salicyl         | 350    | 0.1     | 8.0             | 67.4      | 97.2     |
| n-Nonaldehyde | n-Nonyl alcohol | 300    | 0.1     | 7.0             | 56.0      | 95.1     |

Table 1. Hydrogenation of Carbonyl Compounds Catalyzed by the InNi$_3$C$_{0.5}$/Ni-foam Catalyst

The molar ratio of H$_2$ to DMO is 135, and the ratios of H$_2$ to other substrates are 10. The by-products selectivities were summarized in Table S7.

$^a$Weight hourly space velocity (WHSV) of substrates.

$^b$DMO conversion and EG selectivity after 500 h reaction.
carbonyl-to-hydroxyl transformation. Notably, ethylene glycol (EG) is an important commodity chemical, used for polyester manufacture, anti-freeze compounds, and solvents (Yue et al., 2012), and the gas-phase hydrogenation of dimethyl oxalate (DMO) to EG (its commercialization is on the way) is an attractive alternative EG synthesis using syngas (Fenton and Steinwand, 1974) derived from non-oil resources (such as coal, natural gas, and biomass) even from CO₂ through the RWGS reaction. This foam-structured catalyst is capable of completely converting DMO at a high EG selectivity of 96% with a promising stability (Table 1). Moreover, the InNi₃C₀.5/Ni-foam also shows favorable RWGS and CO₂-to-CH₃OH performances that are comparable with those seen with the InNi₃C₀.5/Al₂O₃/Al-fiber (Tables S8 and S9).

DISCUSSION
In summary, we have discovered an outstanding nano-intermetallic InNi₃C₀.5 catalyst system via RWGS-reaction-oriented pre-design combined with atomistic-theoretical calculations and experimental verifications. Practical fiber/foam-structured InNi₃C₀.5 nano-intermetallic catalysts engineered from nano- to macro-scale in one step have been developed, achieving unprecedented performance in the RWGS reaction and showing potential to catalyze CO₂ hydrogenation to CH₃OH. Most notably, such nano-intermetallic catalysts are also highly active, highly selective, and highly particularly stable for the DMO-to-EG process (EG synthesis using syngas derived from non-oil resources even from CO₂ through the RWGS reaction). We anticipate our essay to be a new point closer toward the ultimate goal of catalysis, namely, designing and tailoring the catalysts atom by atom with precise structure, and our findings might lead to commercial exploitation of such kind of nano-intermetallic catalysts for applications in highly efficient reduction of CO₂ to CO as well as carbonyl-to-hydroxyl transformation.

Limitations of the Study
The large-scale H₂ production should be from the renewable solar, hydraulic, and wind energy.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.07.006.

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AUTHOR CONTRIBUTIONS
P.C., G.Z., X.-R.S., and Y.L. conceived the idea for the project and designed the experiments; P.C., G.Z., X.-R.S., and Y.L. carried out the interpretation and wrote the manuscript; P.C., J.Z., and J.D. conducted the material synthesis, characterizations, and catalysis tests; P.C. and X.-R.S. performed the structural analysis and modeling; X.-R.S. carried out the DFT calculations; all authors discussed and commented on the manuscript; Y.L. directed the research.

DECLARATION OF INTERESTS
Y.L., P.C., J.Z., and G.Z. have a patent application related to this work filed with the Chinese Patent Office on 15 October 2017 (201710956080.1). The authors declare no competing interests.

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Supplemental Information

Nano-Intermetallic InNi$_3$C$_{0.5}$

Compound Discovered as a Superior Catalyst for CO$_2$ Reutilization

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Figure S1. RWGS performance of intermetallic In-Ni catalysts, related to Figure 1. CO$_2$ conversion, product selectivity, and CO-formation rate for different catalysts (GHSV of 30,000 mL g$_{cat}$$^{-1}$ h$^{-1}$, 500 °C, H$_2$/CO$_2$/N$_2$ molar ratio of 66/22/12, 0.1 MPa).
Figure S2. Gibbs free energies ($\Delta G$) as a function of temperature and pressure for the carburization of InNi$_3$ in CO atmosphere ($2\text{InNi}_3 + 2\text{CO}_{(g)} = 2\text{InNi}_3\text{C}_{0.5} + \text{CO}_2_{(g)}$), related to Figure 1.
Figure S3. Geometry, apparent activation energy, morphology, and structural features of the thin-felt InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst, related to Figure 2. (A) XRD patterns of the catalyst precursor of In$_2$O$_3$-NiO/Al$_2$O$_3$/Al-fiber (black) and the fresh catalyst sample (red). (B) N$_2$ adsorption-desorption isotherms (insert: Barrett-Jovner-Halenda (BJH) mesopore size distribution) of the fresh catalyst sample. (C) Size distribution of the InNi$_3$C$_{0.5}$ nanoparticles of the fresh catalyst sample (corresponding to the TEM image in Figure 2C). (D) Arrhenius plot of the RWGS reaction for the InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst (insert: CO-formation rate as a function of reaction temperature). $R^2 = 0.9989$ is the coefficient of determination of the linear regression fitting. Reaction conditions: H$_2$/CO$_2$/N$_2$ = 66/22/12, 1.0MPa, GHSV = 1,810,000 mL g$_{cat}^{-1}$ h$^{-1}$. (E) XRD patterns of the used catalysts samples after stability testing under different conditions (blue: 540 °C, 54,000 mL g$_{cat}^{-1}$ h$^{-1}$, and H$_2$/CO$_2$/N$_2$ = 66/22/12; red: 600 °C, 300,000 mL g$_{cat}^{-1}$ h$^{-1}$, and H$_2$/CO$_2$ = 66/37). (F) SEM image of the used catalyst sample (150 h on stream). TEM images of the used catalysts samples after stability testing under different conditions: (G) 540 °C, 54,000 mL g$_{cat}^{-1}$ h$^{-1}$, and H$_2$/CO$_2$/N$_2$ = 66/22/12; (H) 600 °C, 300,000 mL g$_{cat}^{-1}$ h$^{-1}$, and H$_2$/CO$_2$ = 66/37, (inserts: size distribution of the InNi$_3$C$_{0.5}$ nanoparticles). Note: The N$_2$ adsorption-desorption isotherms and BJH size distribution in (B) reveal the mesoporous feature of the InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst. The average TEM particle size in (C) was derived by statistical counting of 226 InNi$_3$C$_{0.5}$-nanoparticles in the InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst.
Figure S4. Distribution of four C atoms in the eight body-centers, related to Figure 3. (A) 1 × 1 × 1 unit cell of InNi$_3$C. (B) 2 × 2 × 2 super cell of In$_8$Ni$_{24}$C$_8$. (C) Six possible configurations for four C-atoms distribution. **Note:** A 1 × 1 × 1 unit cell of InNi$_3$C was built, which contains one In atom and three Ni atoms, and the In and Ni positions can be identified with the corner-position of In atom and face-centered position of Ni atom (Figure S4A). Notably, this unit cell is composed of InNi$_3$C rather than InNi$_3$C$_{0.5}$. Subsequently, a 2 × 2 × 2 super cell of In$_8$Ni$_{24}$C$_8$ was further built, which contains eight In atoms, twenty-four Ni atoms, and eight C atoms (Figure S4B). For the InNi$_3$C$_{0.5}$ intermetallic, however, this super cell contains eight In atoms, twenty-four Ni atoms, and four C atoms. Namely, there are only four C atoms occupy these eight body-centers. There are six possible configurations for the four C-atoms distribution. The most stable structure is shown as the “V” with the lowest energy (Figure S4C), which is also shown in Figure 3B. This kind of structure can be explained by the distribution of C atoms: the more even C atoms are distributed, the more stable the bulk structure is. In the “V” structure, four C atoms form a regular tetrahedron with each C-C distance of 5.345 Å.
Figure S5. HAADF-STEM analysis, related to Figure 3. (A) Top view of TEM (A) and HAADF-STEM (B) images as well as the corresponding element mappings (C,D) of the InNi$_3$C$_{0.5}$ intermetallic catalyst.
Figure S6. Calculation model and electronic property, related to Figure 4. (A) Top view of the In-Ni-terminated InNi₃C₀.₅(111) surface. (B) 2D view of the charge-density difference for C addition to form InNi₃C₀.₅(111), the cutting plane is the topmost Ni-atoms plane. Blue (negative value) and red (positive value) represent charge depletion and charge accumulation, respectively. The unit for the color scale bar is e Å⁻³. The charge-density difference map shows that there is a degree of charge accumulation at the dual active sites (i.e., 3Ni-In and 3Ni-C) on the InNi₃C₀.₅(111) surface. The results reflect the fact that the dual active sites are potentially electron donors and much more nucleophilic than the other sites. As such, the dual active sites are more favorable for CO₂ activation than other sites on the InNi₃C₀.₅(111) surface.
Figure S7. Possible typical pathways for the RWGS reaction on the InNi$_3$C$_{0.5}$(111) surface, related to Figure 4. (A) Reaction mechanism network (Porosoff et al., 2016; Daza and Kuhn, 2016). Pathway 1, redox route; pathway 2, formate route; pathway 3, carboxyl route. (B) Energy profiles for possible pathways. The energies are reported relative to CO$_2$(g) + H$_2$(g). 

**Note:** CO$_2$* dissociation or CO$_2$* to HCOO* and COOH*? The CO$_2$* dissociated into O* and CO* is energetically favorable (with reaction energy $E_a$, -0.38 eV) and has a low activation barrier ($E_a$, 0.32 eV). The as-formed O* is preferably adsorbed on h1 (3Ni-In) sites, and CO* on h2 (3Ni-C) sites. In contrast, CO$_2$* hydrogenation to formate (HCOO*) or to carboxyl (COOH*) will overcome much higher $E_a$ (0.42 eV for HCOO* and 0.75 eV for COOH*). Clearly, the CO$_2$* dissociation to CO* and O* (i.e., redox pathway) is preferred over the formate and carboxyl pathways on the InNi$_3$C$_{0.5}$(111) surface. O* react with H* to form H$_2$O. The h1-adsorbed O* reacts with H* adsorbed at neighboring h2 site to form OH*, which is also energetically favorable (-0.50 eV) and overcomes a relatively low $E_a$ of 0.73 eV (Table S5). Once OH* is formed, their combination occurs easily to form H$_2$O* (this step is both thermodynamically and kinetically favorable as the reaction is exothermic with a small $E_a$ of 0.25 eV), which is finally desorbed into gas phase ($E_a$, 0.35 eV).
Figure S8. Crystal structure model of Cu and reaction pathways for the RWGS reaction, related to Figure 4. (A) Model of the optimized crystal structure of Cu(111) (left: crystal bulk structure model; middle: top view; right: side view). The reference data for Cu crystal structure is provided in Table S10. The zone marked by the green dashed line on the stable surface (with the lowest surface free energy) is the surface slab structure unit. The atoms comprising the possible active sites in the zone are labeled by numbers. Green dashed line of T_Cu is the Cu termination. (B) Energy profiles for the most favorable pathways for the RWGS reaction on the Cu(111) surface. The energies are relative to CO_2(g) + H_2(g). Relevant adsorption configurations are provided in Figure S9.
Figure S9. Elementary steps involved in the RWGS reaction on the Cu(111) surface, related to Figure 4 and Figure S8. The structures of initial, transition, and final states of all adsorbed species in each elementary step and the corresponding bond length (Å) are shown in this figure (top: side views, bottom: top views). C, H, O, and Cu atoms are shown in grey, white, red, and bronze spheres, respectively. The calculated reaction energies and activation barriers are given in Table S11.
Figure S10. Energy profiles for CO$_2$ hydrogenation to CH$_3$OH and CH$_4$ on the InNi$_3$Ga$_0.5$(111) surface, related to Figure 4. For every elementary step, three possibilities were considered, including H addition to the C-end, H addition to the O-end, and C-O bond cleavage. The energies are reported relative to CO$_2$(g) + 4H(g). A* represents the adsorption state of A on the active sites at infinite separation and (A+B)* represents the most stable co-adsorption state of A and B. Relevant adsorption configurations are provided in Figure S11 and relevant reaction energies ($E_a$) and activation barriers ($E_r$) for each elementary step are provided in Table S5. The pathway in purple is the most favorable for the CO* hydrogenation to CH$_2$OH* and continuous hydrogenation to CH$_3$OH. The pathway in navy from the step of “CH$_3$OH*+O+5H*” is the most favorable for the CO$_2$* hydrogenation to CH$_4$. According to a much lower activation barrier in the competitive elementary steps, the most favorable pathways, for CH$_3$OH/CH$_4$ formation as well as CO-formation are shown in Figure 4C. To improve legibility, “H*” is omitted from the labels after the initial state. The pathway in purple is for the HCO* hydrogenation to CH$_2$OH* and continuous hydrogenation to CH$_3$OH*. The pathway in dark blue from the step of “CH$_3$OH* + O*” is for the CH$_2$OH* decomposition to CH$_3$* and continuous hydrogenation to CH$_4$*. The elementary steps in green are associated with the individual rate-limiting step in the corresponding pathway. Note: Is CO* hydrogenated into CH$_3$OH or CH$_4$? The generated CO* is either desorbed into the gas phase or further hydrogenated into CH$_3$OH and/or CH$_4$. For CH$_3$OH formation, the involved steps are as follows: CO* is first hydrogenated with H* to HCO* by overcoming an $E_a$ of 1.05 eV, and this step is endothermic by +0.92 eV; subsequently, HCO* is hydrogenated to CH$_3$O* by overcoming a small $E_a$ of 0.32 eV, and this step is endothermic by +0.02 eV; CH$_2$O* is hydrogenated into CH$_3$OH* ($E_a$, 0.65 eV), and this step is exothermic; CH$_2$OH* is further hydrogenated into CH$_3$OH* ($E_a$, 0.88 eV), and this step is also exothermic ($E_r$, -0.40 eV). Clearly, the rate-limiting step in CH$_3$OH formation on the InNi$_3$Ga$_0.5$(111) surface is CO*-to-HCO* with an $E_a$ of 1.05 eV. For CH$_4$ formation, the involved steps are as follows: CO* is first hydrogenated with H* to HCO* by overcoming an $E_a$ of 1.05 eV, and this step is endothermic by +0.92 eV; subsequently, HCO* is hydrogenated to CH$_3$O* by overcoming a small $E_a$ of 0.32 eV, and this step is endothermic by +0.02 eV; for methanation, it is necessary to form CH$_x$* ($x = 0$-3) species form CH$_3$O* or CH$_3$OH* species via C-O bond scission, and the CH$_3$OH*...
decomposition to CH₂* has a significantly lower $E_a$ of 0.46 eV (4.39 eV for CO*-to-C*, 1.35 eV for HCO*-to-CH*, 1.02 eV for CH₂O*-to-CH₂*, and 1.48 eV for CH₃O*-to-CH₃*) and is slightly exothermic with an $E_r$ of -0.08 eV (+3.10 eV for CO*-to-C*, +0.55 eV for HCO*-to-CH*, +0.35 eV for CH₂O*-to-CH₂*, and +0.66 eV for CH₃O*-to-CH₃*, see detailed results in Figure S10 and Table S5); CH₂* further hydrogenation to CH₃* is energetically favorable ($E_r$, -0.68 eV) and needs to overcome an $E_a$ of 0.63 eV; the hydrogenation of CH₃* to CH₄* will overcome an $E_a$ of 1.27 eV. Clearly, the rate-limiting step in the methanation on the InNi₃C₀.₅(111) surface is CH₃*-to-CH₄* with an $E_a$ of 1.27 eV. The above comparison clearly suggests that CO* is hydrogenated into CH₃OH (rate-limiting step $E_a$ of 1.05 eV) rather than CH₄ (rate-limiting step $E_a$ of 1.27 eV). Therefore, InNi₃C₀.₅ has relatively higher methanol selectivity than methane selectivity. The results are consistent with the experimental results as well. Moreover, the generalized formation energy ($E_f$) can be employed to evaluate the adsorption strength of the reaction intermediates on InNi₃C₀.₅(111) surface (i.e., the smaller the value, the stronger the adsorption). $E_f$ for CH₂O* is 0.14 eV, 0.99 eV smaller than that for CH₂OH*, indicating CH₂O* is more stable than CH₂OH* on the InNi₃C₀.₅(111) surface (Table S4). Therefore, the lower stability of CH₂OH* makes itself a better intermediate for methanol synthesis than CH₂O*, which has high stability and may not be efficient as transient species in the CH₂O*-to-CH₃OH* conversion. Consistently, this view is also reported in the available literature (Graciani et al., 2014), where authors showed that the high stability of formate (the intermediate over their catalyst) on the catalyst surface makes itself inefficient for CH₂OH synthesis. Therefore, it is rational to conclude that CO₂ hydrogenation to CH₃OH on the InNi₃C₀.₅(111) surface is through the CO*-to-HCO*-to-CH₂O*-to-CH₂OH*-to-CH₃OH* pathway (see detailed results in Table S5).
Figure S11. Elementary steps involved in CO₂ hydrogenation on the InNi₃C₀.₅(111) surface, related to Figure 4. The configurations of initial, transition, and final states of all adsorbed species in each elementary step and the corresponding bond lengths (Å) are shown in this figure (top: side views, bottom: top views). C, H, O, In, and Ni atoms are shown in grey, white, red, bronze, and blue spheres, respectively. The calculated generalized formation energies ($E_f$) and geometric parameters of the intermediates are given in Table S4. The calculated reaction energies and activation barriers for each step are given in Table S5.
Figure S12. Thermodynamic analysis, related to Figure 4. (A) Gibbs free energies ($\Delta G$) and (B) thermodynamic equilibrium composition of the main gaseous products of the RWGS reaction as a function of temperature with an initial stoichiometric H$_2$/CO$_2$ molar ratio of 3/1 and an amount of 100 moles of CO$_2$ at various reaction pressure (0.1-10 MPa).
Figure S13. Standard Gibbs free energy ($\Delta G^\theta_{\text{des}}$) change of CO desorption from InNi$_3$Co$_{0.5}$(111) as the function of temperature, related to Figure 4. $\Delta G^\theta_{\text{des}}$(CO) = $\Delta E_{\text{des}}$(CO) + $G^d$(T), where $G^d$(T) includes the contributions from translation, vibration, and rotation of the CO molecule in gas phase. In this paper, $G^d$(T) is calculated by Dmol$^3$ software (Delley, 1990; Delley, 2000). What to be noted is that increasing temperature is thermodynamically favorable for CO* desorption (Figure S12) due to the significant entropy contributions (Graciani et al., 2014) (that is, the smaller the $\Delta G^\theta_{\text{des}}$(CO), the easier the CO desorption). Therefore, CO* is preferentially desorbed into gas phase at our real RWGS temperature of 420-600 °C (Figure 2D-F).
Figure S14. Structured InNi$_3$C$_{0.5}$/Ni-foam catalyst and its performance for the hydrogenation of DMO to EG, related to Table 1. (A) Optical photograph (left), low-magnitude SEM image (middle), and high-magnitude SEM image (right) of the InNi$_3$C$_{0.5}$/Ni-foam catalyst, showing the engineering of this catalyst at “macro-meso-nano” triple-scale levels. (B) XRD patterns of the In$_2$O$_3$-NiO/Ni-foam catalyst precursor (black) and InNi$_3$C$_{0.5}$/Ni-foam catalyst (red). The JCPDS profile (i.e., vertical lines) from the Joint Committee on Powder Diffraction File database is displayed for reference: InNi$_3$C$_{0.5}$ (No. 28-0468).
### Table S1. Comparison of the InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst with the reported catalysts for RWGS reaction, related to Figure 2.

| Catalyst | T (°C) | P (MPa) | H/C Ratio | GHSV (mL g$_{\text{cat}}$ h$^{-1}$) | $X_{\text{CO}_2}$ (%) | $S_{\text{CH}_4}$ (%) | $S_{\text{CO}}$ (%) | TOS$^a$ (h) | TOF (s$^{-1}$) | Ref. |
|----------|--------|---------|-----------|---------------------------------|-------------------|----------------|----------------|-------------|-------------|------|
| InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber | 540 | 1.0 | 3.0 | 54,000 | 52.5 | 0.5 | 99.5 | 150 | 11.0 | This work |
| 1%Cu/β-Mo$_2$C | 600 | 0.1 | 2.0 | 300,000 | 38.5 | 0.8 | 99.2 | 40 | N/A | Zhang et al., 2017 |
| 36%Cu/ZnO/Al$_2$O$_3$ | 600 | 0.1 | 2.0 | 300,000 | 38.0 | 4 | 96 | 15 | N/A | Wu et al., 2015 |
| 10%Cu-0.3%Fe/Al$_2$O$_3$ | 600 | 0.1 | 1.0 | 60,000 | 14.9 | ~1 | ~99 | 120 | N/A | Gonçalves et al., 2017 |
| 2.4%Ni/nSiO$_2$ | 660 | 0.1 | 4.0 | 40,000 | 67.5 | 1.3 | 98.7 | 40 | N/A | Yang et al., 2017 |
| 0.3%Pt/K$_{80}$-LTL zeolite | 500 | 0.1 | 1.0 | 30,000 | 27.4 | ~0 | ~100 | N/A | 2.25$^b$ | |
| 1.6%Ru@mSiO$_2$-N | 400 | 0.1 | 4.0 | 15,000 | 23.0 | 61.5 | 83.5 | 50 | 0.053 | Dou et al., 2017 |
| 0.4%Ru@mSiO$_2$-A | 400 | 0.1 | 4.0 | 15,000 | 13.7 | 29.6 | 70.4 | N/A | 0.127 | |
| Mo$_2$C | 300 | 0.1 | 3.0 | 36,000 | 8.7 | 6.5 | 93.5 | 36 | 0.43 | |
| 7.5%Co-Mo$_2$C | 300 | 0.1 | 3.0 | 36,000 | 9.5 | 2.0 | 98.0 | 36 | 0.27 | Daza and Kuhn, 2016 |
| Pt-Co/CeO$_2$ | 300 | 0.1 | 3.0 | 36,000 | 6.6 | 18.2 | 81.8 | N/A | 0.24 | |
| Cu-Ni/γ-Al$_2$O$_3$ | 600 | 0.1 | 1.0 | 2,000 | 28.7 | 20.3 | 79.7 | N/A | N/A | Liu and Liu, 1999 |
| Fe-Mo/γ-Al$_2$O$_3$ | 600 | 1.0 | 1.0 | 30,000 | ~35 | ~0 | ~100 | 60 | N/A | Kharaji et al., 2013 |
| 6.2%Pd-3.6%Fe/SiO$_2$ | 450 | 0.1 | 4.0 | 6,120 | 44.7 | 2.8 | 97.2 | N/A | N/A | Park and McFarland, |
| 6.2%Pd-3.6%Ni/SiO$_2$ | 450 | 0.1 | 4.0 | 6,120 | 50.5 | 89.0 | 11.0 | N/A | N/A | 2009 |
| Catalyst                        | Temperature | Load | pH | Activity | Selectivity | Turnover | N/A | N/A | Xu et al., 2015 |
|--------------------------------|-------------|------|----|----------|-------------|----------|-----|-----|----------------|
| Cu/Mo2C                         | 300         | 2.0  | 5.0| 9,000    | 19          | 38.0     | 32.0| N/A | N/A           |
| 1%Ni/Mg(Al)O                    | 700         | 0.1  | 3.0| 540,000  | ~54         | ~6       | ~94 | N/A | N/A           |
| 0.1%Ir/TiO2                     | 350         | 0.1  | 1.0| 6,000    | ~2.1        | ~0       | ~100| N/A | N/A           |
| Cu/Zn@C-submm                   | 500         | 0.1  | 3.0| 18,000   | 5.0         | ~0       | ~100| 20  | N/A           |
| Cu-Zn/AC                        | 500         | 0.1  | 3.0| 18,000   | 4.0         | N/A      | N/A | 11  | N/A           |
| 4.5%Fe/γ-Al2O3                  | 500         | 0.1  | 1.0| 10,000   | 33.5        | <1       | >99 | 15  | N/A           |
| 4.2%Fe-3.4%K/γ-Al2O3            | 500         | 0.1  | 1.0| 20,450   | 22.5        | <1       | >99 | 8   | N/A           |
| Cu/ZnO (C-Z 40-60)              | 230         | 0.1  | 1.0| 520      | 3.6         | N/A      | N/A | N/A | N/A           |
| 2%K-Mo2C/γ-Al2O3                | 300         | 2.1  | 3.0| 7,560    | 11.7        | ~5       | ~95 | 68  | N/A           |
| Fe2O3 nanowires                 | 750         | 0.1  | 1.0| N/A      | 50          | ~0       | ~100| N/A | N/A           |
| Fe2O3 nanosheets                | 510         | 0.1  | 1.0| N/A      | 30          | ~0       | ~100| N/A | N/A           |
| Ce1,1Cu1                        | 400         | 0.1  | 1.0| 60,000   | 37          | ~0       | 100 | 10  | N/A           |
| Cu-ZnGaZrO                      | 325         | 0.1  | 3.0| 3,000    | 16.8        | 0.3      | 99.7| N/A | N/A           |
| NbC                             | 300         | 0.1  | 2.0| 36,000   | 2.09        | 0.5      | 94.5| N/A | 1.0           |
| Mo2C                            | 300         | 0.1  | 2.0| 36,000   | 4.67        | 0.7      | 99.3| N/A | 1.1           |
| WC                              | 300         | 0.1  | 2.0| 36,000   | 3.30        | 4.7      | 95.3| N/A | 0.98          |
| 1%Pt/TiO2                       | 400         | 0.1  | 1.5| 12,000   | 21          | 12       | 88  | N/A | 0.137         |
| PtCo/TiO2                       | 300         | 0.1  | 2.0| 36,000   | 8.2         | 1.2      | 98.8| N/A | 0.588         |
| PtCo/CeO2                       | 300         | 0.1  | 2.0| 36,000   | 9.1         | 7.7      | 92.3| N/A | 0.333         |
| PtCo/ZrO2                       | 300         | 0.1  | 2.0| 36,000   | 7.8         | 10.5     | 89.5| N/A | 0.267         |

Table S1 (Continued)
| Catalyst                        | T | t | N   | TOF | N/A | N/A | 10 | N/A | Ref               |
|--------------------------------|---|---|-----|-----|-----|-----|----|-----|------------------|
| CuFe/Al$_2$O$_3$               | 700| 0.1| 1.0 | 60,000 | 42 | N/A | N/A| 10 | N/A | Zhao et al., 2017 |
| Pt-Co/MCF-17                   | 300| 0.55| 3.0 | 60,000 | ~5 | ~0  | ~99| N/A | N/A | Alayoglu et al., 2011 |
| (1%NiO/CeO$_2$)/50% SBA-15    | 650| 0.1| 1.0 | N/A | 41.8| 3.0 | 97.0| N/A | 0.189 | Alayoglu et al., 2015 |
| (1%NiO/CeO$_2$)/50% SBA-750   | 750| 0.1| 1.0 | N/A | 47.1| 0   | 100| N/A | 0.217 |
| (1%NiO/CeO$_2$)/50% SBA-900   | 900| 0.1| 1.0 | N/A | 55.0| 0   | 100| N/A | 0.250 |

$^a$TOS: time on stream.

$^b$The experiment for TOF calculations was measured at 400 °C.
Table S2. Crystal structure and crystallographic information file of InNi₃C₀.₅, related to Figure 3.

| Crystal structure information | Space group number | Space group | ICSD code | Crystal structure | a (Å)  | b (Å)  | c (Å)  |
|------------------------------|--------------------|-------------|-----------|-------------------|--------|--------|--------|
|                              | 221                | Fm̅3m       | 1897469   | Cubic(fcc)        | 3.780  | 3.780  | 3.780  |

| Crystal element information | Name | Elem. | X       | Y       | Z       | Biso. | S.O.F. | Wyckoff |
|------------------------------|------|-------|---------|---------|---------|-------|--------|---------|
|                              | C1   | C     | 0.00000 | 0.00000 | 0.00000 | 0.5000| 0.5000 | 1a      |
|                              | In1  | In    | 0.50000 | 0.50000 | 0.50000 | 0.5000| 1.0000 | 1b      |
|                              | Ni1  | Ni    | 0.50000 | 0.00000 | 0.00000 | 0.5000| 1.0000 | 3d      |

*a* Face centred cubic (fcc) structure.

*b* DFT calculated values.

*c* Spatial occupied frequency.
Table S3. Surface free energies ($\gamma$, J m$^{-2}$) of the selected surfaces with different terminations$^{a}$, related to Figure 4.

| Surface | Structure (side view) | Termination$^b$ | Surface energy (J m$^{-2}$) |
|---------|-----------------------|------------------|-----------------------------|
| 001$^c$ | ![001 structure](image) | In-Ni            | 1.83                        |
|         |                       | C-Ni             | 1.91                        |
| 011$^d$ | ![011 structure](image) | Ni               | 2.16                        |
|         |                       | In-Ni-C          | 2.24                        |
| 111$^e$ | ![111 structure](image) | In-Ni$^f$        | 1.66$^i$                    |
|         |                       | C$^g$            | 2.19                        |
|         |                       | In-Ni$^h$        | 2.25                        |

$^a$Surface free energy is used to evaluate the stability of the surfaces with different terminations.  
$^b$Different terminations of the corresponding surfaces.  
$^c$InNi$_3$C$_0.5$(001) surface has two kinds of terminations: In-Ni layer and C-Ni layer.  
$^d$InNi$_3$C$_0.5$(011) surface has two kinds of terminations: Ni layer and In-Ni-C layer.  
$^e$The periodic structure of InNi$_3$C$_0.5$(111) has three layers: In-Ni layer, C layer, and In-Ni layer (notably, this In-Ni layer followed by the next In-Ni layer rather than C layer).  
$^f$InNi$_3$C$_0.5$(111) surface is terminated with In-Ni layer followed by C layer.  
$^g$InNi$_3$C$_0.5$(111) surface is terminated with C layer followed by In-Ni layer.  
$^h$InNi$_3$C$_0.5$(111) surface is terminated with In-Ni layer followed by the next In-Ni layer.  
$^i$The InNi$_3$C$_0.5$(111) surface with In-Ni termination and C sub-layer has the lowest $\gamma$ of 1.66 J m$^{-2}$ among all the considered low-index surfaces with different terminations, which indicates that it has the highest stability, consistent with the fact that the InNi$_3$C$_0.5$(111) surface offers the strongest XRD-diffraction intensity and the most preferable exposure in TEM image (Figure 3A,D,E).
Table S4. Generalized formation energies ($E_f$) and optimized geometric parameters of the reaction intermediates on the InNi$_3$C$_{0.5}$(111) surface, related to Figure 4.

| Species   | Site$^a$ | $E_f$ (eV)$^b$ | Bond length (Å) |
|-----------|---------|---------------|-----------------|
| H*        | h$_1$(h$_2$) | -0.94(-0.12)  | $d_{(Ni-H)} = 1.73,1.73,1.73$ (d$_{(Ni-H)} = 1.78,1.78,1.79$) |
| CO$_2^*$  | h$_1$   | 1.70          | $d_{(Ni-C)} = 1.93/d_{(Ni-O)} = 2.02,2.03/d_{(C-O)} = 1.37,1.21$ |
| CO*       | h$_1$(h$_2$) | 0.75(1.42)    | $d_{(Ni-C)} = 1.98,1.98,1.98/d_{(C-O)} = 1.20$ (d$_{(Ni-C)} = 2.00,2.00,2.00/d_{(C-O)} = 1.19$) |
| HCOO*     | b1      | 0.95          | $d_{(Ni-O)} = 1.96,1.96/d_{(C-O)} = 1.27,1.27$ |
| HCOOH*    | t$_1$   | 1.34          | $d_{(Ni-O)} = 2.07/d_{(C-O)} = 1.24,1.21$ |
| COOH*     | h$_1$   | 1.35$^c$      | (d$_{(Ni-C)} = 2.03,2.08/d_{(Ni-O)} = 2.03/d_{(C-O)} = 1.28,1.37$)$^c$ |
| O*        | h$_1$   | -0.14         | $d_{(Ni-O)} = 1.88,1.88,1.88$ |
| OH*       | h$_1$   | -0.73         | $d_{(Ni-O)} = 1.99,1.99,1.99$ |
| H$_2$O*   | t$_1$   | -0.34         | $d_{(Ni-O)} = 2.20$ |
| HCO*      | h$_1$   | 1.55          | $d_{(Ni-O)} = 2.00,2.02/d_{(Ni-O)} = 1.97/d_{(C-O)} = 1.30$ |
| CO*       | h$_1$   | 1.44          | $d_{(Ni-C)} = 1.91,1.92,1.87/d_{(C-O)} = 1.34$ |
| CH$_2$O*  | h$_1$   | 1.42          | $d_{(Ni-C)} = 1.90/d_{(Ni-O)} = 2.15,2.15,2.50/d_{(C-O)} = 1.34$ |
| HCOH*     | h$_1$   | 1.58$^e$      | (d$_{(Ni-C)} = 1.97,1.97,2.09/d_{(C-O)} = 1.39$)$^e$ |
| CH$_3$O*  | h$_1$   | 1.68$^f$      | (d$_{(Ni-C)} = 1.97,1.93/d_{(Ni-O)} = 2.20/d_{(C-O)} = 1.44$)$^f$ |
| CH$_2$OH* | h$_1$   | 0.14          | $d_{(Ni-O)} = 1.98,1.99,2.00/d_{(C-O)} = 1.44$ |
| CH$_3$OH* | h$_1$   | 1.13          | $d_{(Ni-C)} = 2.05,2.18/d_{(Ni-O)} = 2.10/d_{(C-O)} = 1.48$ |
| CH$_4^*$  | t$_1$   | 0.65          | $d_{(Ni-O)} = 2.14/d_{(C-O)} = 1.45$ |
| CH*       | h$_1$   | 1.19          | $d_{(Ni-C)} = 1.89,1.90,1.90$ |
| CH$_2^*$  | h$_1$   | 0.79          | $d_{(Ni-C)} = 1.97,1.97,2.04$ |
| CH$_3^*$  | h$_1$   | 0.00          | $d_{(Ni-C)} = 2.15,2.15,2.16$ |
| CH$_4^*$  | Ph      | -0.16         | --

$^a$Figure 4A shows the detailed structures of these active sites: h$_1$ is Hollow(3Ni-In), h$_2$ is Hollow(3Ni-C), t$_1$ is top(Ni), b$_1$ is bridge(Ni-Ni). “ph” represents the physical adsorption.

$^b$Generalized formation energies are relative to CH$_4$, H$_2$O, and H$_2$ in the gas phase (Medford et al., 2015). Such kind of energy can be employed to evaluate the adsorption strength of the reaction intermediates on InNi$_3$C$_{0.5}$(111) surface. The smaller the value is, the stronger the adsorption. For the species $i$ in the gas phase, $E_{fi}$ is calculated according to the following equation: $E_{fi} = (E_{total})_{fi} - \sum_j n_j R_j$, where $E_{fi}$ is the “generalized formation energy” of species $i$, $(E_{total})_{fi}$ is the total energy of species $i$, $n_j$ is the number of atomic species $j$ in $i$, and $R_j$ is the reference energy of
that atomic species. The reference energies ($R_j$) for each atomic species including atomic C, H and O are calculated by: $R_H = 0.5(E_{total})_{f,H_2}$, $R_C = (E_{total})_{f,CH_4} - 4R_H$, $R_O = (E_{total})_{f,H_2O} - 2R_H$. For the species $i$ on the InNi$_3$C$_{0.5}$(111) surface, $E_{f,i}$ is calculated by $E_{f,i} = (E_{total})_{f,i} - (E_{total})_{f,clean-surface} - \sum_j n_j R_j$, where $(E_{total})_{f,clean-surface}$ is the total energy of the clean InNi$_3$C$_{0.5}$(111) surface.

$^c$COOH* is in cis-form configuration on h1 site.

$^d$COOH* is in trans-form configuration on h1 site.

$^e$HCOH* is adsorbed on h1 site with only C atom connecting with Ni.

$^f$HCOH* is adsorbed on h1 site with C and O atoms connecting with Ni.
Table S5. Reaction energies ($E_r$) and activation barriers ($E_a$) for each elementary step involved in the CO$_2$ hydrogenation on the InNi$_3$C$_0.5$(111) surface, related to Figure 4 and Figures S10,S11.

| Entry | Elementary step | $E_r$ (eV) | $E_a$ (eV) |
|-------|-----------------|------------|------------|
|       |                 | Dual sites$^a$ | Sole h1 sites$^b$ | Dual sites$^a$ | Sole h1 sites$^b$ |
| 1$^e$ | CO$_2$*+*→CO*+O* | -0.38       | -1.10       | 0.32        | 0.32        |
| 2     | CO*→CO$_2$+*    | +1.36       | +2.09       | --          | --          |
| 3$^f$ | CO$_2$*+H*→HCOO*++ | -0.62(-0.61) | +0.19       | 0.42(0.43) | 1.23        |
| 4$^f$ | CO$_2$*+H*→COOH*++ | -0.36(-0.20) | +0.60       | 0.75(0.91) | 1.71        |
| 5$^f$ | O*+H*→OH*++     | -0.50(-0.44) | +0.35       | 0.73(0.79) | 1.58        |
| 6$^f$ | OH*+H*→H$_2$O*++ | +0.50(+0.53) | +1.33       | 1.45(1.49) | 2.28        |
| 7     | OH*+OH*→H$_2$O*+O* | -0.19$^c$    | +0.56$^d$  | 0.25$^e$    | 0.99$^d$  |
| 8$^f$ | CO*+H*→HCOO*++  | +0.92(0.95)  | +1.75       | 1.05(1.08) | 1.88        |
| 9$^f$ | CO*+H*→COH*++   | +0.81(+0.84) | +1.64       | 1.83(1.86) | 2.66        |
| 10$^f$ | HCO*+H*→HCOH*++ | +0.19(+0.17) | +0.98       | 1.11(1.09) | 1.90        |
| 11$^f$ | HCO*+H*→CH$_2$O*++ | +0.02(+0.02) | +0.81       | 0.32(0.32) | 1.11        |
| 12$^f$ | CH$_2$O*+H*→CH$_2$OH*++ | -0.41(-0.14) | +0.66       | 0.65(0.92) | 1.73        |
| 13$^f$ | CH$_2$O*+H*→CH$_3$O*++ | -1.21(-1.13) | -0.33       | 0.60(0.68) | 1.48        |
| 14$^f$ | CH$_3$O*+H*→CH$_3$OH*++ | +0.58(+0.60) | +1.41       | 1.71(1.73) | 2.05        |
| 15$^f$ | CH$_2$OH*+H*→CH$_3$OH*++ | -0.40(-0.38) | +0.43       | 0.88(0.90) | 1.71        |
| 16$^a$ | CO*++→C*+O*     | +3.10       | +1.72       | 4.39        | 4.39        |
| 17$^a$ | HCO*++→CH*+O*    | +0.55       | -0.51       | 1.35        | 1.35        |
| 18$^a$ | CH$_2$O*++→CH$_2$*+O* | +0.35       | -0.77       | 1.02        | 1.02        |
| 19$^a$ | CH$_2$OH*++→CH$_2$*+OH* | -0.08       | -1.07       | 0.46        | 0.46        |
| Entry | Reaction | $E_r$ | $E_a$ | $E_r$ | $E_a$ |
|-------|----------|-------|-------|-------|-------|
| 20$^e$ | CH$_3$O*++$\rightarrow$CH$_3$*+O* | +0.66 | -0.28 | 1.48  | 1.48  |
| 21$^f$ | CH*++H* $\rightarrow$CH$_2$*++ | -0.27(-0.26) | +0.54 | 0.22(0.23) | 1.03 |
| 22$^f$ | CH$_2$*+H* $\rightarrow$CH$_3$*++ | -0.68(-0.64) | +0.16 | 0.63(0.67) | 1.47 |
| 23$^f$ | CH$_3$*+H* $\rightarrow$CH$_4$*++ | -0.11(-0.01) | +0.79 | 1.27(1.37) | 2.17 |

$^a$ $E_r$ and $E_a$ correspond to the reactions that occur on dual active sites.

$^b$ $E_r$ and $E_a$ correspond to the reactions that occur on sole h1 sites.

$^c$ $E_r$ and $E_a$ correspond to the reaction that two OH* on dual active sites.

$^d$ $E_r$ and $E_a$ correspond to the reaction that two OH* on sole h1 sites.

$^e$ For the steps in entries 1,20, the O* preferably occupies the most favorite h1 sites while CO* and CH$_3$* preferably occupy h2 sites and Ni-top sites, respectively, ensuring that the species in this co-adsorption manner have the lowest energies.

$^f$ For the hydrogenation steps (entries 3-6,8-15,21-23), the intermediates are adsorbed on h1, and hydrogenated with the H* that is adsorbed on adjacent h2 sites (the $E_r$ and $E_a$ correspond to the data outside parentheses; there is an interaction between intermediates and H* for this case) or distant h2 sites (the $E_r$ and $E_a$ correspond to the data inside parentheses; there is no interaction between intermediates and H* for this case).

$^g$ For the steps in entries 16-19, the CH$_x$* (x = 0-2) species preferably occupy the most favorite h1 sites while O* or OH* preferably occupy 2Ni-In sites, ensuring that the species in this co-adsorption manner have the lowest energies.
Table S6. CO₂ hydrogenation to methanol, catalyzed by the InNi₃C₀.5/Al₂O₃/Al-fiber catalyst\textsuperscript{a}, related to Figure 5.

| T (°C) | CO₂ Conv. (%) | Product Distribution (mol %) | STY\textsubscript{MeOH}\textsuperscript{b} (g\textsubscript{MeOH} kg\textsubscript{cat}⁻¹ h⁻¹) |
|--------|---------------|-----------------------------|-----------------------------------------------|
| 200    | 1.1           | 97.5 0 2.5 0.0              | 72.8                                          |
| 250    | 2.6           | 89.5 0 10.5 0.0             | 157.9                                         |
| 275    | 4.3           | 83.1 0.3 16.6 0.0           | 242.6                                         |
| 300    | 8.1           | 60.2 0.6 39.2 0.0           | 331.0                                         |

\textsuperscript{a}Reaction conditions: 4.0 MPa, H₂/CO₂/N₂ molar ratio of 66/22/12, GHSV of 21,600 mL g\textsubscript{cat}⁻¹ h⁻¹.

\textsuperscript{b}STY\textsubscript{MeOH} is the space time yield of CH₃OH.
Table S7. By-products selectivity for the hydrogenation of carbonyl compounds to alcohols catalyzed by the InNi$_3$C$_{0.5}$/Ni-foam catalyst, related to Table 1.

| Substrate      | Target product | By-product selectivity                                                                 |
|----------------|----------------|---------------------------------------------------------------------------------------|
| DMO            | EG             | Methyl glycolate, 2-3%; Ethanol, <0.4%; Others (2-methoxyethanol, 2-ethoxyethanol, 1,2-propanediol, and 1,2-butanediol) 1-2%; Gaseous carbon-containing products (including methane, ethylene, ethane, and dimethyl ether), <0.1% |
| Acetone        | Isopropanol    | Propane, 1.0%                                                                         |
| Furfural       | Furfuryl alcohol | Tetrahydrofurfuryl alcohol, 3.9%; 2-methylfuran, 5.1%                                   |
| Cyclohexanone  | Cyclohexanol   | Cyclohexane, 1.0%                                                                      |
| Butanone       | Butanol        | Butane, 1.9%                                                                          |
| Salicylaldehyde | Salicylol     | Benzene and benzyl alcohol, 2.8%                                                        |
| $n$-Nonaldehyde | $n$-Nonyl alcohol | C$_3$-C$_7$ alkanes, 4.9%                                                                    |
**Table S8. Performance of the InNi$_3$C$_{0.5}$/Ni-foam catalyst for the RWGS reaction$^a$, related to Table 1.**

| T (°C) | CO$_2$ Conv. (%) | Product Distribution (mol %) | $r_{CO}^b$ (mmol g$_{cat}^{-1}$ min$^{-1}$) |
|--------|------------------|-------------------------------|------------------------------------------|
|        |                  | CH$_3$OH  | CH$_4$  | CO     | C$_2+$  |                                        |
| 360    | 18.5             | 36.0      | 0.5     | 63.5   | 0.0     | 0.42                                   |
| 420    | 35.6             | 10.2      | 1.0     | 88.8   | 0.0     | 1.12                                   |
| 480    | 45.2             | 3.4       | 2.6     | 94.0   | 0.0     | 1.50                                   |
| 540    | 51.6             | 0.5       | 4.2     | 95.3   | 0.0     | 1.74                                   |

$^a$Reaction conditions: 1.0 MPa, H$_2$/CO$_2$/N$_2$ molar ratio of 66/22/12, 21,600 mL g$_{cat}^{-1}$ h$^{-1}$.

$^b$r$_{CO}$ is the formation rate of CO per gram catalyst per minute.
Table S9. CO₂ hydrogenation to methanol, catalyzed by the InNi₃C₀.₅/Ni-foam catalyst, related to Table 1.

| T (°C) | CO₂ Conv. (%) | Product Distribution (mol %) | STY<sub>MeOH</sub><sup>b</sup> (g<sub>MeOH</sub> kg<sub>cat</sub>⁻¹ h⁻¹) |
|-------|---------------|-----------------------------|----------------------------------|
|       |               | CH₃OH | CH₄    | CO   | C₂⁺  |                      |
| 200   | 0.9           | 98.5  | 0.0    | 1.5  | 0.0  | 60.2                  |
| 250   | 2.5           | 94.2  | 0.6    | 5.2  | 0.0  | 159.9                 |
| 275   | 4.9           | 83.6  | 1.0    | 15.4 | 0.0  | 278.1                 |
| 300   | 7.8           | 57.6  | 1.8    | 40.6 | 0.0  | 305.0                 |

<sup>a</sup>Reaction conditions: 4.0 MPa, H₂/CO₂/N₂ molar ratio of 66/22/12, 21,600 mL g<sub>cat</sub>⁻¹ h⁻¹.

<sup>b</sup>STY<sub>MeOH</sub> is the space time yield of CH₃OH.
Table S10. Reference data for Cu crystal structure in the present study, related to Figure 4 and Figure S8.

| Chemical structure | Crystal structures | International Crystal Structure Database (ICSD) reference |
|--------------------|--------------------|----------------------------------------------------------|
|                    | Space group number | Space group | ICSD code | Crystal structure | a (Å) | b (Å) | c (Å) |
| Cu                 | 225                | Fm$\bar{3}$m | 9008468   | Cubic(fcc)$^a$    | 3.615 | 3.615 | 3.615 |
|                    |                    |             |           |                 | (3.601)$^b$ | (3.601)$^b$ | (3.601)$^b$ |

$^a$Face centred cubic (fcc) structure.

$^b$DFT calculated values.
Table S11. Reaction energies ($E_r$) and activation barriers ($E_a$) for each elementary step involved in the RWGS reaction on the Cu(111) surface, related to Figure 4 and Figures S8,S9.

| Entry | Elementary step | $E_r$ (eV) | $E_a$ (eV) |
|-------|-----------------|------------|------------|
| 1     | $\text{CO}_2^{*}+*\rightarrow\text{CO}^{*}+\text{O}^{*}$ | +1.06      | 1.55       |
| 2     | $\text{CO}_2^{*}+\text{H}^{*}\rightarrow\text{COOH}^{*}+^{*}$ | +0.30      | 1.60       |
| 3     | $\text{CO}_2^{*}+\text{H}^{*}\rightarrow\text{HCOO}^{*}+^{*}$ | -0.55      | 0.67       |
| 4     | $\text{HCOO}^{*}+\text{H}^{*}\rightarrow\text{HCOOH}^{*}+^{*}$ | +0.11      | 0.79       |
| 5     | $\text{HCOOH}^{*}+^{*}\rightarrow\text{HCO}^{*}+\text{OH}^{*}$ | +1.09      | 1.60       |
| 6     | $\text{O}^{*}+\text{H}^{*}\rightarrow\text{OH}^{*}+^{*}$ | -0.92      | 0.62       |
| 7     | $\text{OH}^{*}+\text{H}^{*}\rightarrow\text{H}_2\text{O}^{*}+^{*}$ | -0.27      | 1.07       |
Transparent Methods

Preparation of catalysts

In-Ni nano-intermetallics. The In-Ni nano-intermetallics (InNi, InNi₂, and InNi₃) were prepared using nickel nitrate (Ni(NO₃)₂·6H₂O) and indium nitrate (In(NO₃)₃·2H₂O) as precursors by tuning their corresponding molar ratios. Taking the InNi₃ synthesis as an example, In(NO₃)₃·2H₂O (0.373 g) and Ni(NO₃)₂·6H₂O (0.873 g) were dissolved in distilled water (0.500 g), and the solution was then continuously stirred at ambient temperature for 2 h followed by aging at ambient temperature overnight and further at 100 °C for 24 h. The as-obtained sample was calcined in static air at 400 °C for 2 h to obtain the In₂O₃-NiO precursor, which was directly reduced in a quartz tube (inner diameter of 8 mm) in H₂ flow (flow rate of 30 mL min⁻¹) at atmospheric pressure and 500 °C for 2 h. Finally, the InNi₃ nano-intermetallic was obtained. The InNi and InNi₂ nano-intermetallics were synthesized by the same procedures via tuning the In: Ni molar ratios.

InNi₃C₀.₅ nano-intermetallic. The as-prepared InNi, InNi₂, or InNi₃ was packed in a quartz tube (inner diameter of 8 mm) and carburized in a simulated atmospheric reverse water-gas shift (RWGS) stream of a mixture of H₂ and CO (60 mL min⁻¹, H₂:CO molar ratio of 2:1) at 500 °C for 2 h. The resulting product was slowly cooled to room temperature in a N₂ stream.

InNi₃C₀.₅/Al₂O₃/Al-fiber catalyst. The microfibrous-structured Al₂O₃/Al-fiber support was first prepared from the thin-sheet (ca. 1.3 mm in thickness) 3D network structure of Al-fiber (consisting of 10 vol% 60-μm Al-fiber and 90 vol% void volume) according to the method described elsewhere (Wang et al., 2016). The as-prepared Al₂O₃/Al-fiber support was incipiently impregnated with an aqueous solution of In(NO₃)₃·2H₂O and Ni(NO₃)₂·6H₂O (In: Ni molar ratio of 1:3), followed by drying in air at 100 °C for 12 h and calcining in static air at 400 °C for 2 h to obtain the catalyst precursor In₂O₃-NiO/Al₂O₃/Al-fiber. The In₂O₃-NiO/Al₂O₃/Al-fiber was packed into a quartz tube (inner diameter of 8 mm) and reduced in a H₂ flow (30 mL min⁻¹) at 500 °C for 2 h and carburized at the same temperature in a simulated atmospheric RWGS stream of a mixture of H₂ and CO (60 mL min⁻¹, H₂:CO molar ratio of 2:1) for 2 h.

InNi₃C₀.₅/Ni-foam catalyst. The monolithic NiC₂O₄/Ni-foam was first prepared by the hydrothermal method from the thin-sheet (ca. 1.1 mm in thickness) 3D network structure of Ni-foam (110 pores per inch). Oxalic acid di-hydrate (H₂C₂O₄·2H₂O) and ammonium chloride (NH₄Cl) were separately dissolved in deionized water, mixed together under continuous magnetic stirring, and transferred into a stainless steel Teflon-lined autoclave of 100 mL capacity. The Ni-foam was placed into the autoclave, which was then sealed and maintained at 150 °C for 2 h. The as-obtained NiC₂O₄/Ni-foam was incipiently impregnated with an aqueous solution of In(NO₃)₃·2H₂O followed by drying in air at 100 °C for 12 h and calcined in static air at 400 °C for 2 h to obtain the catalyst precursor In₂O₃-NiO/Ni-foam. The In₂O₃-NiO/Ni-foam was reduced and carburized under the same conditions as the InNi₃C₀.₅/Al₂O₃/Al-fiber catalyst.

Characterization of catalysts

X-ray diffraction. XRD measurements were conducted to analyze the structure and crystallinity of the as-prepared nano-intermetallics and catalysts (i.e., InNi, InNi₂, InNi₃, InNi₃C₀.₅, InNi₃C₀.₅/Al₂O₃/Al-fiber, and InNi₃C₀.₅/Ni-foam). The XRD patterns were collected on a Rigaku Ultima IV diffractometer using a Cu Kα radiation source (λ = 1.5405 Å) operating at 35 kV and 25 mA in the 2θ angle range of 10-100° using a step size of 0.02° and at a scanning speed of 30° min⁻¹.

Elemental analyses. The In: Ni molar ratios of InNi, InNi₂, InNi₃, and InNi₃C₀.₅ were determined to be 1:0.99, 1:2.01, 1:2.98, and 1:2.99, respectively, by inductively coupled plasma emission spectrometry (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. Carbon element analysis was performed on a PerkinElmer 2400 CHN elemental analyzer, and the In: Ni:C
molar ratio of InNi$_3$C$_{0.5}$ was determined to be 1:2.99:0.49. Moreover, the carbon content in
InNi$_3$C$_{0.5}$ was further confirmed by thermogravimetric analysis (TGA) on a Mettler-Toledo Model
TGA/SDTA851e apparatus. In the TGA measurement, the In$_2$O$_3$-NiO mixture (10.0014 mg with
In: Ni molar ratio of 1:3) was reduced in H$_2$ flow at 500 °C for 2 h (these reduction conditions
ensure the full transformation of In$_2$O$_3$-NiO into InNi$_3$ (8.0160 mg)), and the as-obtained InNi$_3$
was then carburized in a simulated atmospheric RWGS stream of H$_2$/CO mixture (60 mL min$^{-1}$
with H$_2$:CO molar ratio of 2:1) at 500 °C for 2 h (these carburization conditions ensure the full
transformation of InNi$_3$ into InNi$_3$C$_{0.5}$ (8.1810 mg)). According to the weight increment from
InNi$_3$ to InNi$_3$C$_{0.5}$, the carbon content was determined to be 0.1650 mg, so that the In: Ni:C molar
ratio was determined to be 1:3:0.49, consistent with the above determined In: Ni: C molar ratio of
1:2.99:0.49.

**Transmission electron microscopy.** TEM measurements were performed on a Tecnai G$^2$ F30
high-resolution transmission electron microscope. The sample was suspended in ethanol by ultrasonication, and a drop of the suspension was deposited onto a holey carbon foil supported on a copper grid. The grids were left to dry at room temperature prior to TEM measurements. The accelerating voltage was 200 kV.

**Scanning electron microscopy.** SEM measurements were performed on a Hitachi S-4800
scanning electron microscope (Japan) with an accelerating voltage of 3.0 kV.

**Nitrogen adsorption-desorption.** Nitrogen adsorption-desorption isotherms were measured at -196 °C on a Quantachrome Autosorb-3B instrument (USA). The samples were evacuated at 300 °C for at least 6 h before adsorption-desorption. The specific surface area (SSA) was calculated from the adsorption branch in the range of relative pressure from 0.05 to 0.25 by the Brunauer-Emmett-Teller (BET) method. The pore size distribution and total pore volume were determined using the Barrett-Joyner-Halenda (BJH) model from the adsorption branch of the isotherms.

**In-situ Fourier transform infrared spectroscopy (FTIR).** In-situ FTIR experiments in the
continuous flow of H$_2$/CO$_2$/N$_2$ (molar ratio of 66/22/12) were recorded on a Nicolet NEXUS 6700
spectrometer (USA), equipped with a mercury-cadmium-telluride (MCT) detector and a high
temperature transmission cell rigid with CaF$_2$ windows. Spectra were acquired at a resolution of
4 cm$^{-1}$ and 32 scans, and analyzed using OMNIC software. In a typical steady testing, the sample
was pressed to a wafer (13 mm in diameter) and placed into the cell chamber. The sample wafer
was pretreated at 400 °C for 2 h in the H$_2$ flow, flushed with highly purified N$_2$ at 400 °C for 1 h
and cooled down to 50 °C in N$_2$ for taking a reference spectrum. Then the reaction gas of
H$_2$/CO$_2$/N$_2$ (66/22/12) was introduced into the in-situ chamber at 50 °C and FTIR spectra were
recorded continuously for 32 scans with 2 spectra per minute until it reached steady state. For the
CO$_2$ hydrogenation, FTIR spectra were recorded continuously to capture dynamic change of the
surface species in the cell chamber temperature range from 50 to 325 °C with a ramping rate of
2 °C min$^{-1}$.

In order to analyze the composition of the products from in-situ FTIR experiment, all possible
carbonaceous species were detected by the on-line mass spectrometer (Proline Dycor, AMETEK
Process Instrument, USA) and the corresponding mass signals (intensities of ions with m/z of 44
(CO$_2$), 31 (CH$_3$OH), 28 (CO), and 16 (CH$_4$)) were recorded.

**Evaluation of Catalysts**

**Reverse water-gas shift reaction.** Catalysts were evaluated in a continuous flow fixed-bed
tubular reactor made of stainless steel with aluminum liner pipe (inner diameter of 8 mm with
length of 768 mm) that was heated by a furnace. Six thermocouples, located at the upper, middle,
and bottom of the furnace wall and reactor wall, were used to ensure the homogeneity of the
temperature in the reaction zone. In a typical catalyst evaluation, the circular chips of the
InNi$_3$C$_{0.5}$/Al$_2$O$_3$/Al-fiber catalyst (0.500 ± 0.002 g) were packed layer-by-layer into the reactor.
The catalyst bed at the center of the reactor was supported by quartz wool at both ends, while the
remaining space was filled with quartz powder. Before evaluating their performance, the as-prepared catalysts were pre-treated in an atmospheric H₂ flow (30 mL min⁻¹) at 400 °C for 2 h. The reactant gas (H₂/CO₂/N₂ mixture with a molar ratio of 66/22/12 and N₂ as the internal standard) was introduced into the reactor using calibrated mass flow controllers. The reaction temperature, pressure, and gas hourly space velocity (GHSV) were varied in the range of 420-600 °C, 1.0-4.0 MPa, and 21,600-54,000 mL g⁻¹ cat h⁻¹, respectively. The catalyst stability was tested under severe RWGS reaction conditions: 540 °C, GHSV of 54,000 mL g⁻¹ cat h⁻¹, H₂/CO₂/N₂ molar ratio of 66/22/12, and 1.0 MPa; 600 °C, GHSV of 300,000 mL g⁻¹ cat h⁻¹, H₂/CO₂ molar ratio of 66/33, and 0.1 MPa.

The product stream was quantitatively analyzed by an online Agilent 7820 gas chromatograph (GC) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). The post-reactor line was heated to 120 °C to prevent product from condensing. All the data were collected after a given reaction time (at least 3 h) under steady-state conditions. A gas sample was withdrawn every 30 minutes, and more than eight-times measurements were taken for each reaction parameter. The products from this reaction were CO, CH₄, CH₂OH, C₂H₄, C₂H₆, and C₃H₆. The total content of C₂H₄, C₂H₆, and C₃H₆ was less than 0.1% and was, thus, neglected. The CO₂ conversion (%) and product selectivity (%) were calculated by the standard normalization method on the basis of carbon atom balance according to the following equations:

\[
\text{CO}_2 \text{ conversion (})% = \left(1 - \frac{f_{\text{CO}_2A_{\text{CO}_2,\text{out}}}}{\sum f_iA_{i,\text{out}} + f_{\text{CO}_2A_{\text{CO}_2,\text{out}}}}\right) \times 100%
\]

\[
i \text{ selectivity (})% = \left(\frac{f_iA_{i,\text{out}}}{\sum f_iA_{i,\text{out}}}\right) \times 100%
\]

where \(A_{i,\text{out}}\) and \(f_i\) are the chromatographic peak area at the outlet and the relative molar calibration factor of the individual product \(i\) (\(i\): CO, CH₄, and CH₂OH), respectively.

**Methanol synthesis.** The reaction apparatus, evaluation procedure, and product analyses for the methanol synthesis from CO₂ hydrogenation were the same as for the RWGS reaction described above. The reaction temperature was varied in the range of 200-300 °C at 4.0 MPa and GHSV of 21,600 mL g⁻¹ cat h⁻¹.

Space time yield of methanol (STY), expressed as grams of CH₃OH per kilogram catalyst per hour (gCH₃OH kg⁻¹ cat h⁻¹), was calculated according to the following equation:

\[
\text{CH}_3\text{OH STY} = \frac{F_{\text{CO}_2,\text{in}} \times X_{\text{CO}_2} \times S_{\text{CH}_3\text{OH}} \times MW_{\text{CH}_3\text{OH}}}{W_{\text{cat}} \times V_m}
\]

where \(F_{\text{CO}_2,\text{in}}\) is the volumetric flow rate (mL h⁻¹), \(X_{\text{CO}_2}\) is the CO₂ conversion, \(S_{\text{CH}_3\text{OH}}\) is the CH₂OH selectivity, \(MW_{\text{CH}_3\text{OH}}\) is the molecular weight of CH₃OH (32 g mol⁻¹), \(W_{\text{cat}}\) is the overall mass of catalyst (kg), and \(V_m\) is the ideal molar volume of CO₂ at standard temperature and pressure.

**Dimethyl oxalate (DMO) hydrogenation to ethylene glycol (EG).** Catalysts were evaluated in a continuous flow fixed-bed tubular stainless-steel reactor with 8 mm inner diameter. The InNi₃Co₅/Ni-foam catalyst (0.500 ± 0.002 g) was loaded into the reactor and heated to the desired reaction temperature, and then H₂ was introduced into the reactor until the pressure was raised to the set points and the DMO methanol solution (13 wt%) was simultaneously introduced into the reactor. The DMO methanol solution was pumped using a high-pressure advection pump. The molar ratio of H₂ to DMO, weight hourly space velocity (WHSV_DMO), and reaction pressure were varied in the range of 45-180, 0.22-0.88 g DMOM g⁻¹ cat h⁻¹, and 0.5-3.5 MPa, respectively. The catalyst stability was tested under the following conditions: 210 °C, molar ratio of H₂ to DMO of 90, WHSV_DMO of 0.44 g DMOM g⁻¹ cat h⁻¹, and 2.5 MPa.

Only trace amounts (less than 0.1%) of gaseous carbon-containing products (methane, ethylene, ethane, and dimethyl ether) were formed, which were neglected in the product distribution calculations. The liquid effluent was collected and analyzed using a Shimadzu 2014C...
GC with a FID detector and a HP-INNOWax column. The products from this reaction were EG, methyl glycolate, ethanol, 2-methoxyethanol, 2-ethoxyethanol, 1,2-propanediol, and 1,2-butanediol. The DMO conversion (%) and product selectivity (%) were calculated according to the following equations:

\[ \text{DMO conversion} = \left(1 - \frac{f_{\text{DMO, out}}}{\sum f_i A_{\text{out}} + f_{\text{DMO, out}}} \right) \times 100\% \]

\[ i \text{ selectivity} = \left(\frac{f_i A_{\text{out}}}{\sum f_i A_{\text{out}}} \right) \times 100\% \]

where \( A_{\text{out}} \) and \( f_i \) are the chromatographic peak area at the outlet and the relative molar calibration factor of the individual product \( i \) (\( i = \text{EG, methyl glycolate, ethanol, 2-methoxyethanol, 2-ethoxyethanol, 1,2-propanediol, and 1,2-butanediol} \), respectively.

Computational details

Methods. All spin-calculation were performed using the plane-wave-based periodic density functional theory (DFT) method as implemented in the Vienna \textit{ab initio} simulation package (VASP), and the electron-ion interaction was described by the projector augmented wave (PAW) method (Kresse and Furthmüller, 1996a; Kresse and Furthmüller, 1996b). To elucidate the role of the van der Waals interaction in this system, we performed vDW-DF calculations using the optB86b functional (Klimeš et al., 2010; Klimeš et al., 2011). The cutoff energy for the plane wave basis set was fixed at 400 eV. Geometry optimization was performed with a conjugate-gradient algorithm and considered to be converged when the forces on each unconstrained atom was 0.03 eV/Å or less. The transition states were determined by the climbing-image nudged elastic band method (CI-NEB) as implemented into VASP using the VTST tool set (Henkelman et al., 2000; Sheppard et al., 2008). All the transition states were confirmed by vibrational analysis to have only one imaginary frequency. Dipole correction was employed in all the calculations.

The surface free energy (\( \gamma \)) was used to determine the thermodynamical stability of the surfaces with different terminations and was calculated according to

\[ \gamma = \frac{E_{\text{slab}} - N E_{\text{bulk}}}{A} \]

where \( E_{\text{slab}} \) is the total energy of the slab, \( N \) is the number of the InNi\textsubscript{3}C\textsubscript{0.5} units in the slab, \( E_{\text{bulk}} \) is the bulk total energy per InNi\textsubscript{3}C\textsubscript{0.5} unit, and \( A \) is the total surface area formed in cleavage (including both slab sides).

Images of the Wulff equilibrium shape of the InNi\textsubscript{3}C\textsubscript{0.5} crystal and electron density difference were obtained using the VESTA software (Momma and Izumi, 2011).

Models. The InNi\textsubscript{3}C\textsubscript{0.5}(111) surface was represented with a \((2 \times 2)\) cell of six layers where three bottom layers were fixed to the bulk geometry while the upper layers together the adsorbates were allowed to relax (Figure 4A). Cu\text{1(111)} surface was modelled with a \((3 \times 3)\) surface unit cell of four layer thicknesses (Figure S8A). During optimization, the top two layers together with the adsorbed species were allowed to relax. The Monkhorst-Pack grids of \((3 \times 3 \times 3)\) and \((4 \times 4 \times 4)\) \(k\)-points were employed for the Cu and InNi\textsubscript{3}C\textsubscript{0.5} bulk, respectively. The Monkhorst-Pack grids of \((3 \times 3 \times 1)\) and \((4 \times 4 \times 1)\) \(k\)-points were employed for the Cu\text{1(111)} and InNi\textsubscript{3}C\textsubscript{0.5}(111) surfaces, respectively. The vacuum spacing was greater than 15 Å to avoid cross-talk effects because of the periodical repetition of the unit cells. The size of the unit cell, the thickness of the layers, and the precision thresholds used in our calculations were carefully checked, and the structural parameters and adsorption energies had high accuracies of 0.01 Å and 0.01 eV, respectively.

Active sites analyses. The zone marked by the green lines is the surface slab structure unit on the corresponding stable surface (i.e., with the lowest surface free energy). The atoms comprising the possible active sites in the corresponding zones are labeled by numbers (Figure 4A and Figure S8A). As shown in Figure S8A, four kinds of active sites were established on the Cu\text{1(111)} surface: one top site (Cu1), one bridge site (Cu1-Cu2), one \textit{fcc} site (Cu1-Cu3-Cu4), and one \textit{hcp} site (Cu1-
Cu2-Cu3). Intermediates adsorbed on different sites: CO*, H2O*, and HCOOH* were absorbed at top sites; H*, O* and OH* were absorbed at fcc sites; HCOO*, COOH*, and HCO* were absorbed at bridge sites.

On the InNi3C0.5(111) surface (Figure 4A), nine kinds of active sites were established, including two top sites (Ni1, In2), three bridge sites (Ni1-Ni6, In2-Ni6, Ni3-Ni6), and four hollow sites (Ni1-Ni5-Ni6 (with one In atom right below), Ni1-In2-Ni6, In2-Ni3-Ni6 (with one Ni atom right below), Ni3-Ni4-Ni6 (with one C atom right below)). The sites in yellow/red-triangulations have stable adsorption for most intermediates on the InNi3C0.5(111) surface (Table S4).

**Reaction pathways.** We used the most stably terminated InNi3C0.5(111) surface to investigate the surface reaction pathways for CO2 hydrogenation. For the RWGS reaction, three possible reaction pathways including the redox, carboxyl (COOH) and formate (HCOO) routes were considered.

In order to explore the possibilities in CH3OH/CH4 formation from CO2 hydrogenation on the InNi3C0.5(111) surface, DFT calculations were performed to examine the reaction pathways for the formation of CH3OH and CH4. For every elementary step, three possibilities were considered, including H addition to the C-end, H addition to the O-end, and C-O bond cleavage (Figure S10).

The most favorable pathways, according to a much lower activation barrier in the competitive elementary steps, for CH3OH/CH4 formation as well as CO-formation were shown in Figure 4C.

**Thermodynamic analysis.** The thermodynamic analysis was conducted by using the HSC Chemistry 7.0 software, with the results shown in Figure S12. In the analysis, the temperature was increased from 200 to 700 °C. The species of H2, CO2, CO, H2O, CH4, and CH3OH were simultaneously considered. The formation of CH4 and CH3OH was considered as unwanted side reactions.

**Main reaction**

**Reverse water-gas shift reaction (RWGS):**

\[ \text{CO}_2(g) + \text{H}_2(g) \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}(g); \Delta H^{o}_{298K} = +41.17 \text{ kJ mol}^{-1} \quad (1) \]

**Side reaction**

**Methane formation reaction:**

\[ \text{CO}_2(g) + 4\text{H}_2(g) \leftrightarrow \text{CH}_4(g) + 2\text{H}_2\text{O}(g); \Delta H^{o}_{298K} = -165.0 \text{ kJ mol}^{-1} \quad (2) \]

**Methanol synthesis reaction:**

\[ \text{CO}_2(g) + 3\text{H}_2(g) \leftrightarrow \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g); \Delta H^{o}_{298K} = -49.01 \text{ kJ mol}^{-1} \quad (3) \]

**Rate, turnover frequency of CO-formation, and apparent activation energy for RWGS reaction**

**CO-formation rate.** CO-formation rate, expressed as micro-moles of produced CO per gram InNi3C0.5/Al2O3-Al-fiber catalyst per minute (mmolCO gcat^{-1} min^{-1}), was calculated according to the equation:

\[ r = \frac{F_{\text{CO}_2} \times X_{\text{CO}_2} \times S_{\text{CO}}}{V_m \times W_{\text{cat}}} \]

where \( F_{\text{CO}_2} \) is the flow rate of CO2 (mL min^{-1}), \( X_{\text{CO}_2} \) is the CO2 conversion, \( S_{\text{CO}} \) is the CO selectivity, \( V_m \) is the ideal molar volume of CO2 at standard temperature and pressure, and \( W_{\text{cat}} \) is the mass of the InNi3C0.5/Al2O3-Al-fiber catalyst.

**Turnover frequency of CO-formation.** In order to assess the intrinsic activity of the InNi3C0.5/Al2O3-Al-fiber catalyst for the RWGS reaction, the specific turnover frequency (TOF) was measured (with CO2 conversion of 7.3% at 540 °C, 1.0 MPa, and GHSV of 2,536,000 mL gcat^{-1} h^{-1}) and calculated, which was defined as the produced CO per active-site per second:

\[ \text{TOF} = \frac{r}{\text{Active site number}} = \frac{F_{\text{CO}_2} \times X_{\text{CO}_2} \times S_{\text{CO}} \times N_A}{V_m \times W_{\text{cat}} \times x \times N_{\text{num}}} \]
where \( F_{CO2} \) is the flow rate of CO\(_2\) (mL s\(^{-1}\)), \( X_{CO2} \) is the CO\(_2\) conversion, \( S_{CO} \) is the CO selectivity, \( V_m \) is the ideal molar volume of CO\(_2\) at standard temperature and pressure, \( N_A \) is the Avogadro constant, \( W_{cat} \) is the mass of the InNi\(_3\)C\(_{0.5}\)/Al\(_2\)O\(_3\)/Al-fiber catalyst, \( x \) is the InNi\(_3\)C\(_{0.5}\) loading in the InNi\(_3\)C\(_{0.5}\)/Al\(_2\)O\(_3\)/Al-fiber catalyst, and \( N_{num} \) is the number of available surface active sites (i.e., the total number of 3Ni-In and 3Ni-C) on per gram InNi\(_3\)C\(_{0.5}\).

**Number of available surface active sites.** Assuming a uniform spherical shape of InNi\(_3\)C\(_{0.5}\) nanoparticles, the specific surface area (SA: m\(^2\) g\(^{-1}\)) of the InNi\(_3\)C\(_{0.5}\) nanoparticles in the InNi\(_3\)C\(_{0.5}\)/Al\(_2\)O\(_3\)/Al-fiber catalyst was estimated based on their TEM-visualized particle size according to the following equation (Gao et al., 2017):

\[
SA = \frac{6}{\rho \times d_{1\text{InNi}_3\text{C}_{0.5}}}
\]

where \( \rho \) is the density of bulk InNi\(_3\)C\(_{0.5}\). The corresponding TEM-visualized particle size distribution of InNi\(_3\)C\(_{0.5}\) nanoparticles is shown in Figure S3C.

Notably, the total area of the 3Ni-In and 3Ni-C sites accounted for 20.4\% of the total surface area of InNi\(_3\)C\(_{0.5}\)(111) surface (Figure 4A). Assuming that all exposed surfaces of the supported InNi\(_3\)C\(_{0.5}\) nanoparticles were InNi\(_3\)C\(_{0.5}\)(111) surface, the \( N_{num} \) was calculated according to the following equation:

\[
N_{num} = \frac{SA \times 20.4\%}{A_{(3\text{Ni-In or 3Ni-C})}}
\]

where \( A_{(3\text{Ni-In or 3Ni-C})} \) is the area of one 3Ni-In or 3Ni-C active-site (one 3Ni-In site has equal area to one 3Ni-C site of 3.013 \( \times \) 10\(^{-20} \) m\(^2\)).

**Apparent activation energy.** The activation energy (\( E_a \)) over the InNi\(_3\)C\(_{0.5}\)/Al\(_2\)O\(_3\)/Al-fiber catalyst was calculated based on the Arrhenius plot. According to the Arrhenius equation (\( \ln r = \ln A - \frac{E_a}{RT} \)), \( E_a \) is the slope estimated from the linear relationship of the \( \ln \) function of the CO\(_2\) formation rate with the reciprocal of temperature. For the InNi\(_3\)C\(_{0.5}\)/Al\(_2\)O\(_3\)/Al-fiber catalyst, the RWGS reaction was performed under a kinetic-limiting region by controlling the temperature and GHSV to maintain CO\(_2\) conversion well below the equilibrium conversion (CO\(_2\) conversion less than 15\%). Reaction conditions: \( H_2/CO_2/N_2 = 66/22/12, 1.0 \) MPa, GHSV of 1,940,000 mL g\(_{cat}\)\(^{-1}\) h\(^{-1}\), and temperature in the 420-580 °C range.
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