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Potassium-Promoted Limestone for Preferential Direct Hydrogenation of Carbonates in Integrated CO$_2$ Capture and Utilization

Shuzhuang Sun, Zheng Chen, Yi Kai Xu, Yuanyuan Wang, Yingrui Zhang, Catherine Dejoie, Shaojun Xu, Xin Xu, and Chunfei Wu

**ABSTRACT:** Integrated CO$_2$ capture and utilization (ICCU) via the reverse water–gas shift (RWGS) reaction offers a particularly promising route for converting diluted CO$_2$ into CO using renewable H$_2$. Current ICCU-RWGS processes typically involve a gas–gas catalytic reaction whose efficiency is inherently limited by the Le Chatelier principle and side reactions. Here, we show a highly efficient ICCU process based on gas–solid carbonate hydrogenation using K promoted CaO (K-CaO) as a dual functional sorbent and catalyst. Importantly, this material allows ~100% CO$_2$ capture efficiency during carbonation and bypasses the thermodynamic limitations of conventional gas-phase catalytic processes in hydrogenation of ICCU, achieving >95% CO$_2$-to-CO conversion with ~100% selectivity. We showed that the excellent functionalities of the K-CaO materials arose from the formation of K$_2$Ca(CO$_3$)$_2$ bicarbonates with septal K$_2$CO$_3$ and CaCO$_3$ layers, which preferentially undergo a direct gas–solid phase carbonates hydrogenation leading to the formation of CO, K$_2$CO$_3$, CaO and H$_2$O. This work highlights the immediate potential of K-CaO as a class of dual-functional material for highly efficient ICCU and provides a new rationale for designing functional materials that could benefit the real-life application of ICCU processes.

**KEYWORDS:** carbon dioxide, hydrogenation, selectivity, integrated CO$_2$ capture and utilization, transition-metals free catalysts, reverse water–gas shift reaction, dual functional material

1. INTRODUCTION

The emission of CO$_2$ from using fossil fuels is a significant contributor to climate change.$^1$ However, fossil fuels will still play a dominant role as a source of energy in the near future.$^2$ Although the application of renewable energy (e.g., solar and wind energy) mitigates the challenges related to CO$_2$ emissions, it faces shortcomings of high cost, low generation efficiency, and slow deployment.$^3$ Consequently, upcycling CO$_2$ to store renewable energy and keeping it in the carbon cycle provide practical strategies to address the above challenges. To shorten and simplify the whole CO$_2$ capture and utilization processes, integrated CO$_2$ capture and utilization (ICCU) processes have been proposed and studied.$^4$ In a typical ICCU process, CO$_2$ is first captured and fixed from diluted sources (e.g., flue gas) using sorbents, such as CaO and monoethanolamine.$^5$ Subsequently, the saturated sorbents can be regenerated by converting the adsorbed CO$_2$ into valuable chemicals, such as CO and CH$_4$.$^6$ A wide range of catalytic processes have been attempted for the utilization process in ICCU, such as photocatalytic,$^7$ electrocatalytic$^8$ plasma-catalytic$^9$ and thermo-catalytic$^{10}$ processes (Figure 1d). The ICCU can occur under mild conditions (e.g., room temperature) with the assistance of photo- or electrocatalysts, representing a sustainable concept for reducing CO$_2$ emission. However, they are limited by the low reaction efficiency (Figure 1d) and inhibited by the system complexity in scaling up.$^{11}$ Compared to these processes, the conventional thermo-catalytic ICCU under relatively mild conditions presents a more practical solution to meet the urgent industrial level deployment requirement for carbon neutrality in the CO$_2$ emission point, such as the power plants.$^{12}$

Integrated CO$_2$ capture and reverse water–gas shift (eq 1) reaction (ICCU-RWGS) is a promising route to reduce CO$_2$ into CO using renewable H$_2$. This combined with the
Figure 1. ICCU performances using 20 mol % K-CaO. ICCU schematic diagram and the pivotal reactions using K-promoted CaO (a). The real time (b) and cyclic (c) ICCU performance at 650 °C using 20 mol % K-CaO (carbonation: 15.2% CO2/N2 for 0.5 min; purge: N2 for 3.0 min; hydrogenation: 100% H2 to the end; carbon balance: C1 species during hydrogenation to CO2 capacities during carbonation). (d) Comparison of reported integrated CO2 capture and utilization systems.32,11,14,16,25,26

Fischer–Tropsch process, liquid chemicals with long lifetime can be obtained from CO.26 It was widely believed that the CO2 is captured in the form of carbonates (eq 3) during CO2 capture step and then the gaseous CO2 decomposed from carbonates, react with H2 on the active sites of the catalysts in an integrated hydrogenation step.9,16 Hence, many researchers used the experience of catalyst design from conventional RWGS into ICCU-RWGS to enhance its performance.5,9,16,17 Typically, dual functional materials (DFMs), including active catalytic metals (e.g., Ni or Fe) and adsorbents (e.g., CaO), are widely applied in ICCU.9,21,22 However, due to the Le Chatelier principle-controlled equilibrium of RWGS and the occurrence of side reactions (e.g., eq 2), the performance of ICCU-RWGS is far from ideal. Furthermore, the introduction of active metals would increase the material cost and cause environmental distress.23

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & = \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298K} = +0.42 \text{ eV} \\
\text{CO}_2 + 4\text{H}_2 & = \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K} = -1.71 \text{ eV} \\
\text{CO}_2 + \text{CaO} & \leftrightarrow \text{CaCO}_3 \quad \Delta H_{298K} = -1.86 \text{ eV}
\end{align*}
\]

Our previous study confirmed that CaCO3 could directly react with H2 to generate CO even in the absence of active transition metals (eq 4).24 However, the inevitable CaCO3 decomposition (reverse eq 3) restricted the CO2 conversion (<80%) at the regeneration/utilization stage. A significant amount of effort have been made to optimize RWGS catalytic performance, while there have been comparatively fewer studies that reveal the importance of the direct hydrogenation of carbonates. Here we propose a novel strategy to improve the selectivity of direct hydrogenation of carbonates (e.g., eq 4) by hindering the decomposition process (e.g., reverse eq 3), representing a more direct and effective route for CO2 utilization in ICCU.

\[
\text{CaCO}_3 + \text{H}_2 = \text{CO} + \text{CaO} + \text{H}_2\text{O} \quad \Delta H_{298K} = 2.28 \text{ eV}
\]

Based on the above understanding, we report a transition-metal-free potassium-promoted CaO (K-CaO) DFM synthesized by a simple impregnation method. By introducing potassium into the commercial CaO, we find that the K species participate in the carbonation of CaO and form stable cocarbonates K2Ca(CO3)2 with enhanced reaction kinetics. The generated K2Ca(CO3)2 selectively reacts with H2 rather than decompose to generate CO2. As a result, we record a CO2 conversion rate >95% with ~100% CO selectivity, which outperforms the results of ICCU processes carried out using state-of-the-art active metal (e.g., Ni)-based materials. Combining the experimental characterizations, such as ex-situ synchrotron radiation X-ray diffraction, Raman, and in situ diffused reflectance infrared Fourier transform spectroscopy analysis, with the density functional theory (DFT) calculations, we reveal the key intermediate and mechanism over the K-CaO DFM to facilitate the CO2 conversion and CO selectivity. Importantly, the K-CaO DFM presented here can be easily deployed by using two fluidized reactors for continuous CO2 capture and on-site utilization.

2. RESULTS

The ICCU experiments were carried out in a single tubular fixed-bed reactor (Figure S1), and the carbonation and hydrogenation were realized by switching the inlet gas between simulated flue gas (15.2% CO2/N2) and H2. The K-CaO DFM was obtained by impregnating KNO3 onto CaCO3 and calcining at 800 °C (Figure S2). During the calcination, the KNO3 and CaCO3 were thoroughly decomposed and reformed into K2CO3, CaO, and K2Ca(CO3)2 (fairchildite), respectively (Figure S3 and S4). The commercial CaO reagent was applied as the benchmark material.

As demonstrated in Figure 1b, 20 mol % K-CaO can optimally achieve ca. 100% CO2 removal efficiency at 650 °C in 0.5 min of the carbonation process. Furthermore, the captured CO2 (carbonates) can be isothermally converted into CO with sustainable CO2 conversion (>95%) and CO selectivity (>99.9%) in 50 cycles of ICCU processes (Figure 1c and S5). The uncaptured CO2 in carbonation slightly...
increases from ~0 to 0.008 mmol g\(^{-1}\) after 50 cycles, while the CO\(_2\) conversion only decreases to 94.3% in cyclic hydrogenation, which outperforms CaO (Figure S5d) and the reported ICCU-RWGS using transition-metal-CaO DFMs\(^{8,9,16}\) (Table S1) and other ICCUs using photo, electro or plasma-catalytic processes (Figure 1d). Even the molten salt slowly evaporates (Table S2) and the morphologies of materials slightly change in cyclic ICCU evaluations (Figure S13a). However, the main phase composition and surface species are stable (Figures S13b and c), consistent with outstanding performance stability. Notably, the trace transition-metal impurities (i.e., Fe, Pd, etc., in ppm level, reagents might contribute to the presented performance. However, an impact by Fe is unlikely given previous work\(^{8}\) showing that 10% Fe loading resulted in poorer performance (<85% CO\(_2\) conversion) compared to this work.

In order to demonstrate the superiority of short-term (0.5 min) carbonation and to understand the mechanism, we extended the carbonation time to 30 min. The ICCU performance using 20 mol % K-CaO is displayed in Figure 2a in comparison with the benchmark material of CaO (Figure 2b). Notably, there is an ~1.7 μmol g\(^{-1}\) s\(^{-1}\) CO\(_2\) escape flow using CaO in the initial carbonation stage at 650 °C, which does not occur using 20 mol % K-CaO. Furthermore, the saturated carbonated CaO and 20 mol % K-CaO display vastly different hydrogenation performances. More specifically, the amount of unconverted CO\(_2\) is constant and high (~1.4 μmol g\(^{-1}\) s\(^{-1}\)) using CaO during the hydrogenation of ICCU at 650 °C (Figure 2b), resulting in a limited CO\(_2\) conversion (~75%, Figure S6). In contrast, there are two hydrogenation stages for 20 mol % K-CaO. The \(\alpha\) stage (time on stream, TOS, in the range of 1860−2180 s in Figure 2a) exhibits similar performance with CaO (Figure 2b), while the \(\beta\) stage (TOS of 2180−3300 s in Figure 2a) possesses a low CO\(_2\) flow (<0.2 μmol g\(^{-1}\) s\(^{-1}\)) and considerable CO flow (~2.6 μmol g\(^{-1}\) s\(^{-1}\)), resulting in significantly enhanced CO\(_2\) conversion.

The influences of ICCU temperatures and K loadings were also investigated, as shown in Figures S6 and S7. It was found that the temperature was negatively correlated with the CO\(_2\) capture performance. Specifically, CaO could achieve excellent initial CO\(_2\) removal efficiency at 600 °C (Figure S7a, <0.6 μmol g\(^{-1}\) s\(^{-1}\) CO\(_2\) escape rate). However, the CO\(_2\) capture performance of CaO significantly deteriorates at higher temperatures due to the equilibrium of eq 3 (e.g., Figure 2).

\[\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3\]

\[\text{CaCO}_3 + \text{H}_2 \rightarrow \text{CaHCO}_3 + \text{CO}\]

\[\text{CaHCO}_3 + \text{H}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}\]

\[\text{CaCO}_3 + \text{H}_2 \rightarrow \text{CaHCO}_3 + \text{H}_2\text{O}\]

\[\text{CaHCO}_3 + \text{H}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}\]
There is a trace amount of CaCO$_3$ generation on 20 mol % K-CaO in 0.5 min carbonation, consistent with Raman observation (Figure S15 and Table S3, weak CO$_2^-$ bands at 711 and 1079 cm$^{-1}$). As a benchmark, the CaO sample showed weak CaCO$_3$, XRD peaks after 0.5 min of carbonation (Figures 2d and S16), indicating the slow kinetics of carbonation of CaO (eq 3). K$_2$Ca(CO$_3$)$_2$ is identified as the key species for the 100% CO$_2$ removal efficiency (Figure 2a and S7) during the carbonation using 20 mol % K-CaO. The as-formed K$_2$Ca(CO$_3$)$_2$ might detach from the surface of CaO due to inappropriate crystal structure (Figure S17), and the continuous exposure of CaO contributes to the enhanced CO$_2$ capture. The sufficient carbonation (30 min) then further promotes the formation of K$_2$Ca(CO$_3$)$_2$ (Figures 2c, S14, and S15), accompanied by the enhanced generation of CaCO$_3$. Furthermore, K$_2$Ca(CO$_3$)$_2$ can partly form K$_2$Ca$_2$(CO$_3$)$_3$ by combing with CaCO$_3$ (eq 6).

$$K_2CO_3 + CaO + CO_2 = K_2Ca(CO_3)_2 \tag{5}$$

$$K_2Ca(CO_3)_2 + CaCO_3 = K_2Ca_2(CO_3)_3 \tag{6}$$

After 10 min of hydrogenation (at the β stage in Figure 2a), the 20% K-CaO material presents mainly three crystal phases which can be attributed to K$_2$Ca(CO$_3$)$_2$, K$_2$CO$_3$, and CaO (Figures 2c and S14). It is noted that the consumption of K$_2$Ca(CO$_3$)$_2$ and CaCO$_3$ in the hydrogenation process is fast, which is responsible for the unreacted release of CO$_2$ in the initial time of hydrogenation (α stage in Figure 2a). In contrast, K$_2$Ca(CO$_3$)$_2$ tends to directly react with H$_2$ to generate CO (eq 7) rather than self-decomposition to generate gaseous CO$_2$ (eq 8), which is further evidenced by in situ DRIFTS (Figure 2f, no distinct CO$_2$ generation). Importantly, by the end of the hydrogenation process, the CO$_2$ saturated 20 mol % K-CaO catalyst is completely regenerated to the initial state (K$_2$CO$_3$ + CaO) (Figures 2c and S14) and ready for the next ICCU cycle.

The consumption of carbonates in H$_2$ atmosphere includes decomposition (reverse eq 3 or eq 8) and direct hydrogenation
(eq 4 or eq 7) pathways, which could be illustrated by the isothermal thermogravimetric analysis under a N₂ or H₂ reducing atmosphere (Figure 2e). Consuming carbonate selectively through direct hydrogenation instead of decomposition is a widely overlooked but highly effective way to achieve a high CO₂ conversion during the hydrogenation stage. It was found that the consumption rate of K₂Ca(CO₃)₂ in 5% H₂/Ar (eq 7, k₂) was ~6.1 times faster than its decomposition in N₂ (eq 8, k₁), while the consumption rate of CaCO₃ was only 2.0 times faster in 5% H₂/Ar than in N₂. Compared to CaCO₃, K₂Ca(CO₃)₂ tends to be consumed via direct hydrogenation (eq 7) instead of decomposition (eq 8) in H₂, indicating the high selectivity of direct hydrogenation of K₂Ca(CO₃)₂. In short, as illustrated in Figure S18, K₂Ca(CO₃)₂ is the key contributor to the 100% CO₂ removal efficiency during carbonation due to the enhanced formation kinetics and also the enhanced CO₂ conversion during hydrogenation via selectively converting carbonates through direct hydrogenation to produce CO (eq 7).

K₂Ca(CO₃)₂ + H₂ = K₂CO₃ + CaO + H₂O + CO₂

(eq 7)

K₂Ca(CO₃)₂ = K₂CO₃ + CaO + CO₂

(eq 8)

To further study how K promotes the direct hydrogenation of carbonates to CO, DFT calculations were performed to compare the hydrogenation pathway with the decomposition pathway over CaCO₃, K₂CO₃, and K₂Ca(CO₃)₂ respectively. Since the reaction temperature was relatively high, we assumed that the calculated reaction energies provided a good estimation to compare the preferences of different reaction pathways. As shown in Figure 3a, the CaCO₃ hydrogenation possessed a reaction energy of 1.38 eV to release CO and to form Ca(OH)₂, which was actually observed in the in situ DRIFTs experiment (Figure 2g). The latter could decompose to (CaO + H₂O) easily, as indicated by a further 1.12 eV decomposition energy. Even though the CaCO₃ direct decomposition to (CaO + CO₂) possessed a higher reaction energy of 1.76 eV, the difference was not high enough to avoid the CaCO₃ direct decomposition in opposition to hydrogenation. These calculation results are consistent with the experimental observations that the hydrogenation rate of CaCO₃ (L) was found to be too stable to be decomposed, it could quickly react with CaCO₃(L) with a reaction energy of ~0.73 eV to form bulk Ca(OH)₂ and K₂CO₃. The as-formed Ca(OH)₂ (B) could decompose to generate CaO easily, while bulk K₂CO₃ could react with bulk CaCO₃ to regenerate K₂CO₃(L) and CaCO₃ with a reaction energy of 0.51 eV (Figure 3d). Therefore, DFT calculations suggested that the overall reaction pathway over the K-promoted CaO system involved hydrogenation of K₂CO₃ (L) to produce CO and an intermediate KOH layer on the surface of CaCO₃ (L). Simultaneously, a new K₂CO₃ layer was expected to form on the surface of CaCO₃ (L). The K₂CO₃ layer possesses superior selectivity to direct hydrogenation instead of decomposition and hence contributes to the excellent CO₂ conversion in ICCU-RWGS using K-promoted CaO DFM.

3. DISCUSSION

The ICCU process based on reverse water–gas shift (RWGS) reaction allows CO₂ to be captured directly from flue gas and converted in situ into highly concentrated and valuable syngas. This provides a novel and promising engineering solution for achieving carbon neutrality. Although ICCU could achieve higher CO₂ conversion rates compared to conventional RWGS, it is still restricted by the equilibrium of RWGS. A 20 mol % K-CaO DFM was produced here, exhibiting cyclically sustainable ~100% CO₂ removal efficiency from the flue gas and >95% CO₂ conversion and ~100% CO selectivity in hydrogenation at 650 °C over 50 reaction cycles, which outperforms the state-of-art counterparts. The performance evaluation, characterization, and simulation reveal that the direct gas–solid carbonates hydrogenation dominates in ICCU using K-CaO DFM, while the carbonates decomposition is highly suppressed due to the mainly formed K₂Ca(CO₃)₂ with septal K₂CO₃ and CaCO₃ layers. By improving the selectivity of carbonates direct hydrogenation out of decomposition, the ICCU using K-CaO DFM can bypass the gas–gas phase equilibrium restriction of RWGS, producing high purity syngas for the following applications. This work points out the immense potential of carbonate direct hydrogenation via a gas–solid phase CO₂ conversion pathway in ICCU. Moreover, we show that unwanted side reactions such as the decomposition of carbonates can be hindered by introducing K to form intercalated CaCO₃ bicarbonate layers. The process shown in this work represents a simple and effective strategy for future materials design in ICCU, which is significant for the deployment of ICCU technologies in real-life settings. More broadly, this work provides an alternative route for enhancing the catalytic efficiency of gas–gas phase reactions, which have significant
implications for many other applications in sustainability beyond ICCU.

4. METHODS

4.1. Material Preparation

The potassium-promoted CaO was prepared by wet impregnation with various molar ratios of potassium to calcium. Typically, as illustrated in Figure S2, x mol KNO₃ (0 < x < 0.1, Sigma-Aldrich, >99%) was dissolved in 20 mL distilled water, followed by adding 0.1 = x mol CaCO₃ (Sigma-Aldrich, >99%) into the aqueous solution. The mixture was stirred at room temperature for 1 h and vaporized at 90 °C with continuous stirring and then dried at 110 °C overnight. The dried sample was ground and calcined at 800 °C for 5 h at a heating rate of 5 °C min⁻¹. The obtained sample was named as x mol % K-CaO (X = 1000x, i.e., x = 0.01 for 10 mol % K-CaO).

4.2. Material Characterization

The K loading and Ca content were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using nitric acid digestion. The crystal structures of the materials were tested by powder X-ray diffraction (XRD) on a PANalytical empyrean series 2 diffractometer with a Cu Ka X-ray source. The attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) data were collected using Agilent Cary 630. The Raman spectra were characterized on the WITec Alpha 300R Confocal Raman Microscope reflectance infrared Fourier transform spectroscopy (in situ DRIFTs) and an ASAP 3000 analyzer, and the Brunauer surface area and pore structure of the materials were characterized by dispersive X-ray spectrometer (EDX) on FEI Quanta FEG. The scanning electron microscopy (SEM) images coupled with an energy goniometer head and aligned to the beam spot. The diffraction sealed and mounted on a brass spinner. The sample was attached to a France. The sample was packed into a 0.7 mm capillary that was thermogravimetric analysis was carried out on a Hi-Res TGA 2950.

4.3. Performance Evaluation and Investigation

The ICCU was carried out in a quartz fixed bed reactor. The quartz reaction tube (12 mm OD; 10.5 mm ID and 650 mm length) was fixed in a tube furnace (Elite), and 0.5 g of sample was placed in the middle of the reaction tube and fixed with quartz wool. The mass of sample loading was calibrated by thermogravimetric analysis with 850 °C N₂ calcination to eliminate the mass changes caused by the adsorption of substances in the air. The ICCU evaluation was isothermally carried out under 600, 650, and 700 °C, respectively. The real time gas concentration (CO₂, CO, and CH₄) during ICCU was monitored by an online gas analyzer (KANE AUTOplus 5—2) equipped with a nondispersive Infrared (NDIR) sensor. 15.2% CO₂/ N₂ and 100% H₂ were applied to simulate the flue gas and reducing agent for carbonation and hydrogenation, respectively. Typically, 100 mL min⁻¹ (controlled by mass flow meter; OMEGA FMA-A2000) 15.3% CO₂/N₂ was introduced into the reaction tube for 30 min to demonstrate the CO₂ capture procedure, then 100 mL min⁻¹ N₂ was introduced for 3 min to purge the residual gaseous CO₂ followed by switching into 100 mL min⁻¹ 100% H₂ to achieve the CO₂ generation and regeneration of sorbent. The CO₂ conversion, CO selectivity and CO yield in hydrogenation were calculated by integrating the real-time data during hydrogenation, as shown in the following equations:

\[
X (\text{μmol s}^{-1} \text{ g}^{-1}) = \frac{x (\%) \times 1.667 (\text{μL s}^{-1})}{0.0224 (\text{mL μmol}^{-1}) \times 0.5 (\text{g})}
\]

4.4. Computational Details

All DFT calculations were performed with Vienna ab initio simulation package (VASP)³⁵,³¹ The kinetic energy cutoff for the plane wave basis sets of the valence electrons was set to 400 eV. The core electrons were described by the projector augmented-wave (PAW) method.³² The surface Monkhorst—Pack meshes of 5 × 5 × 5 and 2 × 2 × 1 k-point sampling in the Brillouin zone were employed for the bulk and slab model, respectively. For bulk calculations, all atoms were relaxed, and the lattice constants were optimized. For surface slab modeling, the three bottom atomic layers were fixed while the other atomic layers were relaxed. After the convergence criteria for optimizations were met, the largest remaining force on each atom was less than 0.02 eV Å⁻¹. For all calculations, the generalized gradient approximation (GGA) of the Perdew—Burke—Ernzerhof (PBE) functional³³ was used. The contributions of dispersive interactions were accounted for by using the DFT+D3 method with Becke—Johnson (BJ) damping.³⁴,³⁵ The electronic energy was used for reaction energy calculations, which provided reaction energies of CaCO₃ decomposition to produce CO₂ (1.76 eV) and overall hydrogenation to produce CO and CaO (2.50 eV) comparable to the experimental enthalpies presented in eq 3 (1.86 eV) and eq 4 (2.28 eV).

For calculating the formation energy of the K₂CO₃ layer and the KOH layer, the K₂Ca(CO₃)₂-(001) surface with the CaCO₃ layer ((001)-CaT) as the terminal layer was used. For calculating the formation energy of the CaCO₃ layer, the K₂Ca(CO₃)₂-(001) surface with the K₂CO₃ layer ((001)-KT) as the terminal was used. Using the K₂CO₃ layer as an example, the formation energy, ∆Ef[K₂CO₃(L)], was calculated by

\[
\Delta E_f[K_2CO_3(L)] = (E[nK_2CO_3(L)@001] - CaT) - E[nK_2CO_3(B)] - E[001] - CaT]/n
\]

where n represents the number of K₂CO₃ molecules loaded on the K₂Ca(CO₃)₂-(001) surface, E[nK₂CO₃(B)] is n times of the total energy of bulk K₂CO₃, E[001] − CaT is the total energy of the K₂Ca(CO₃)₂-(001) surface with the CaCO₃ layer as terminal, and E[nK₂CO₃(B)@001] − CaT is the total energy of n K₂CO₃ loaded on the K₂Ca(CO₃)₂-(001) surface with the CaCO₃ layer as terminal.

Additional experimental details, materials characterizations, detailed data evaluation, and spectral assign reference (PDF)
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Notes

The authors declare no competing financial interest.

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REFERENCES


(2) Zou, C.; Zhao, Q.; Zhang, G.; Xiong, B. Energy revolution: From a fossil energy era to a new energy era. Natural Gas Industry B 2016, 3 (1), 1–11.


