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Integrated CO₂ capture and methanation on Ru/CeO₂-MgO combined materials: Morphology effect from CeO₂ support

Shuzhuang Sun, Hongman Sun, Shaoliang Guan, Shaojun Xu, Chunfei Wu

1. Introduction

Global warming and the related severe climate issues caused by the continuous rise of carbon dioxide (CO₂) emissions have attracted significant attention [1]. CO₂ capture and utilization (CCU) is a promising solution to reduce the emission of CO₂ and can be closely integrated with current industrial processes (such as power plants and cement manufacturing). Therefore, extensive researches have been carried out on developing sorbents for carbon capture [2] and catalysts for CO₂ conversion such as CO₂ methanation [3–4], reverse-water–gas shift reaction [5–7], dry reforming of methane [8,9], etc. However, the energy consumption on CO₂ separation, enrichment and transportation significantly increase the overall cost of the CCU process.

Recently, integrated CO₂ capture and utilization (ICCU) using dual-functional combined materials is gaining increasing interest by combining CO₂ adsorption and utilization in a single reaction system [10–12]. ICCU is a gas-swing two-stage system, as shown in Fig. 1. The 1st stage is the CO₂ capture from the diluted CO₂ exhaust gas, and the 2nd stage is CO₂ conversion accompanied by the recovery of absorbents. It is suggested that ICCU has lower energy consumption benefited from the isothermal operating condition and less capital investment on the process units compared with conventional CCU [13]. The key point is that ICCU avoids CO₂ enrichment and transportation steps by in situ converting the fixed CO₂ thus greatly reducing the cost of CCU.

CO₂ methanation, believed as a promising process to recycle CO₂ back to fuel, was applied in the 2nd stage of ICCU in this work. Owing to its exothermic property, CO₂ methanation prefers a moderate reaction temperature (<500 °C). Noble metal-based catalysts (e.g. Ru [3,14], Au [15], and Pd [16]) have been widely used to achieve excellent catalytic performance owing to their outstanding catalytic activity and CH₄ selectivity. Furthermore, it is well known that the interaction between active metals and supports plays a vital role in catalytic processes [15,17], especially for catalysts with reducible supports (e.g. CeO₂ [18,19], TiO₂ [20,21], etc.). The CeO₂ has been widely utilized in various applications, such as biotechnology [22], catalysis [23–25], sensor [26], sorbents [27], etc. Recent studies speculated that the Support-Metal Interaction (SMI) and oxygen vacancies on catalysts are highly relevant to their catalytic performance [28–31]. The
morphologies of supports [32] and the preparation method of catalysts [33] have influences on SMI and oxygen vacancies of supported catalysts, and have been widely studied in terms of the catalytic role of SMI and oxygen vacancy [24,34–36]. Furthermore, the electron transfer between reducible supports and metals is also considered to be important to CO₂ methanation performance (i.e. CH₄ selectivity) [32,37]. As a novel process, the integrated CO₂ capture and methanation (ICCM) has a different catalytic environment from that of traditional CO₂ methanation. And the effect of CeO₂ morphology on the ICCM process worth a comprehensive assessment in relation to CO₂ adsorption and the following catalytic methanation.

\[ CO₂ + 4H₂ = CH₄ + 2H₂O ΔH_{298K} = -252.9 \text{kJ/mol} \] (1)

The ICCM process includes the steps of CO₂ adsorption, product desorption, and the corresponding diffusion of chemicals [16], and requires optimized temperatures to balance these processes and maintain better kinetics and thermodynamics. However, there are few choices of adsorbents that are suitable for moderate-temperature (200–500 °C) CO₂ capture applications. In the previous research, we utilized Li, Na, K-doped MgO as CO₂ adsorbent and achieved acceptable capture performance at 300 °C [38,39], which matches the CO₂ methanation requirement. For the controlled component of catalysts, Ru is selected as the effective catalytic active metal for CO₂ methanation [14,40–42].

Herein, a set of combined materials using Ru/CeO₂ as a catalyst and physical mixed MgO as adsorbent were developed with three different CeO₂ morphologies, including rod, particle, and cube CeO₂, to investigate the effect of CeO₂ support morphology on the ICCM process. In particular, we studied the influence of ceria support on the morphologies, reducibility, SMI and oxygen vacancies of Ru/CeO₂, in relation to CO₂ adsorption and CH₄ production. Furthermore, we investigated the mechanism of ICCM over Ru/CeO₂-MgO by in situ DRIFTS and proposed the ICCM reaction pathways.

2. Experimental section

2.1. Materials preparation

2.1.1. Preparation of CeO₂ supports with different morphologies

Three different CeO₂ supports with the rod, particle, and cube morphologies were produced. The CeO₂ supports with rod and cube morphologies were prepared by a hydrothermal method [18,43]. Typically, 5.21 g Ce(NO₃)₃·6H₂O (>99%, Sigma-Aldrich) was dissolved in deionized water (30 ml) to produce a Ce source solution, and 57.6 g NaOH (>95%, Sigma-Aldrich) was dissolved in deionized water (210 ml) followed by mixing the Ce source solution with NaOH solution to obtain a slurry. After stirring 30 mins at room temperature, the slurry was transferred into Teflon-lined stainless-steel autoclaves and held at 100 and 200 °C for 24 h to obtain rod-CeO₂ and cube-CeO₂ supports, respectively. After the autoclave was cooled to room temperature naturally, the precipitates were separated by vacuum filtration, washed by deionized water and ethanol to neutrality, and dried at 100 °C in air overnight. Particle-CeO₂ was prepared by precipitating ammonia cerium nitrate with urea in an aqueous solution, as reported by Tana et al. [44]. Typically, 60 g of (NH₄)₂Ce(NO₃)₆ (>99%, Sigma-Aldrich) and 200 g of urea (>99%, Sigma-Aldrich) were dissolved into 2000 ml distilled water, and the mixture was heated to 90 °C under stirring and kept at this temperature for 27 h. After filtration and washing with water, the precipitate was dried at 100 °C overnight. All three dried materials were calcined at 600 °C for 5 h with a heating rate of 5 °C min⁻¹ to obtain CeO₂ supports with various morphologies, donated as rod-CeO₂, particle-CeO₂, and cube-CeO₂, respectively.

2.1.2. Preparation of Ru/CeO₂ materials

The Ru/CeO₂ catalysts with 2 wt% Ru was prepared using a wet impregnation method. In general, 1.0 g of CeO₂ powder (rod-CeO₂, particle-CeO₂, or cube-CeO₂) was suspended in 20 ml of Ru³⁺ solution (RuCl₃, 0.01 mol/L) followed by stirring for 24 h at room temperature. The suspension was evaporated and dried at 110 °C overnight and then calcined in air at 300 °C for 2 h with a heating rate of 2 °C min⁻¹, donated as Ru/rod-CeO₂, Ru/particle-CeO₂, and Ru/cube-CeO₂. The samples were reduced in 5% H₂/N₂ at a flow rate of 50 ml min⁻¹ at 300 °C for 3 h (heating rate is 2 °C min⁻¹) to obtain the reduced Ru/CeO₂ catalysts.

2.1.3. Preparation of dual functional combined materials

The Li, Na, K-doped MgO adsorbent was prepared using a method reported by Harada et al. [38]. Firstly, 9.713 g 4MgCO₃·Mg(OH)₂·H₂O (>99%, Sigma-Aldrich), 0.207 g LiNO₃ (>99%, Sigma-Aldrich), 0.153 g NaNO₃ (>99%, Sigma-Aldrich), and 0.526 g KNO₃ (>99%, Sigma-Aldrich) were added into 40 ml deionized water with stirring at room temperature for 60 min. The obtained white slurry was dried at 110 °C overnight and then calcined at 450 °C for 4 h. The combined materials were prepared by physically mixing the Li, Na, K-doped MgO sorbent and the reduced Ru/CeO₂ catalysts in a mortar with a 2:1 mass ratio. The obtained combined materials were donated as Ru/rod-CeO₂-MgO, Ru/particle-CeO₂-MgO, and Ru/cube-CeO₂-MgO, respectively.

2.2. Materials characterization

The elemental analysis of Ru/CeO₂ catalysts was carried out using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The samples were digested by peroxide fusion and then tested by Perkin Elmer PE2400CHNS. Powder X-ray diffraction (PXRD) of all catalysts was measured on a PANalytical Empyrean series 2 diffractometer with Cu Kα X-ray source. And the Scherrer’s equation was used to calculate the average crystallite size of different Ru/CeO₂ samples. Transmission electron microscopy (TEM) was obtained using a JEOL 2100 observing the morphologies and Ru dispersion of reduced Ru/CeO₂.

X-ray photoelectron spectrum (XPS) analysis of Ru/CeO₂ materials was performed using a Thermo Fisher Scientific NEXSA spectrometer fitted with a mono-chromated Al Kα X-ray source (1486.7 eV). The Ru/CeO₂ materials were reduced at 300 °C for 3 h in 5% H₂/N₂ and then protected by Ar in a glove box before XPS analysis to prevent the re-oxidation of oxygen vacancies and reduced Ru in air. Data were recorded at pass energies of 200 eV for survey scans and 50 eV for the high-resolution scan with 1 eV and 0.1 eV step sizes, respectively, at a spot...
size of approximately 400 µm. The charge neutralization of the sample was achieved using a combination of both low-energy electrons and argon ions. C 1 s electron at 284.8 eV was used as a standard reference to calibrate the photoelectron energy shift. All the data analysis was performed on the Casa XPS software (version: 2.3.22PR1.0).

H₂ temperature-programmed reduction (H₂-TPR) was performed by Hi-Res TGA 2950 thermogravimetric analyzer to characterize the reducibility of the Ru/CeO₂ materials. Typically, the samples were pretreated under N₂ at 600 °C for 10 mins and then equilibrated at 50 °C in N₂ followed by raising the temperature to 800 °C at a rate of 10 °C min⁻¹ in 100 ml/min 5% H₂/N₂.

2.3. Integrated CO₂ capture and methanation (ICCM) evaluation

The ICCM performances of Ru/CeO₂-MgO combined materials with different CeO₂ morphologies were carried out in a fixed bed reactor with a stainless-steel tube (8 mm in diameter) at atmospheric pressure. Typically, 0.3 g combined materials was placed in the middle of the reaction tube and fixed by quartz wool, and two thermocouples were used to control the temperature of the combined materials and the furnace, respectively. Omega mass flow controllers (FMA-A2306) were calibrated by a bubble flowmeter and used to control the gas flow. ICCM includes two stages: carbonation reaction (1st stage) and CO₂ methanation (2nd stage). The 1st stage was performed using 35% CO/N₂ at 100 ml/min at 300 °C for 1 h, followed by sample purge in 50 ml min⁻¹ N₂ for 10 min. Then, 5% H₂/N₂ at a 50 ml min⁻¹ flow rate was switched on for the 2nd stage for 30 min isothermally. The exhaust gases coming out of the 2nd stage reactor were collected by a gasbag and analyzed by a GC (HP Hewlett 5890 series II gas chromatograph) with a Restek Shimcarbon ST 100/120 column (2 m, 1 mm ID/1/16 OD Silico). The cycle evaluation was performed with extra 20 mins N₂ purge among each cycle. The yields of CH₄, CO₂, and CO₂ conversion were calculated using the below equations (No CO and other hydrocarbons were detected):

\[ Y_{CH₄} = \frac{V_{CH₄} \times F_{CH₄}}{22.4 \times m_{CH₄}} \]  
\[ Y_{CO₂} = \frac{V_{CO₂} \times F_{CO₂}}{22.4 \times m_{CO₂}} \]  
\[ C_{CO₂} = \frac{Y_{CO₂}}{Y_{CO₂} + Y_{CH₄}} \times 100 \% \]

\[ Y_{CH₄} \text{ (mmol g}^{-1}\text{)}, Y_{CO₂ \text{ (mmol g}^{-1}\text{)}}, \text{ and } C_{CO₂} \] are derived from the GC analysis.

2.4. In situ DRIFTS (diffused reflectance infrared fourier transform spectroscopy) study

The in situ DRIFTS tests of ICCM over Ru/rod-CeO₂ and Ru/rod-CeO₂-MgO were carried out using an Agilent Cary 680 FTIR spectrometer with a liquid N₂ cooled detector. The spectra were recorded with 4 cm⁻¹ resolution, and each spectrum was averaged 128 times. The experimental setup is as follows: The catalysts were pre-treated with He (99.999%, BOC gas Ltd.) at 150 °C for 10 mins to remove the surface adsorbrates and then increase the temperature to reaction temperature of 300 °C. Then H₂ (5% H₂/N₂) was introduced to reduce catalysts for 2 h. Then, switch gas flow to He to remove the residual H₂ for 10 min and collect the background reference signal. The carbonation step was carried out using 35% CO₂/N₂ for 60 mins; the purge step proceeded with He for 9 mins to remove the gas phase CO₂ followed with the regeneration step, which was carried out by switching gas flow to 5% H₂/N₂ for 60 mins. The ICCM of Ru/rod-CeO₂ and Ru/rod-CeO₂-MgO (carbonation-purge-hydrogenation) was tested at 300 °C under atmospheric pressure.

3. Results and discussion

3.1. Characterization of Ru/CeO₂ materials

To investigate the effect of CeO₂ morphologies on ICCM, Ru loading on CeO₂ supports is 1.9% ± 0.13% (Table 1). Fig. 2a shows the XRD patterns of the reduced Ru/CeO₂ catalysts with different CeO₂ morphologies, referring to the standard peak position of hcp-structured Ru (JCPDS 06-0663), tetragonal RuO₂ (JCPDS 40-1290), and cubic-structured CeO₂ (JCPDS 34-0394), respectively. The peaks at 2 Theta of 28.8, 33.3, 47.7, 56.6, 59.4, 69.6, and 76.9 are derived from the CeO₂ lattice plane of (1 1 1), (2 0 0), (2 2 0), (2 2 2), (4 0 0), and (3 1 1) [19,45], respectively. Furthermore, the average crystallite size of CeO₂ in Ru/CeO₂ materials is calculated using the Scherrer equation as 9.0, 6.9, and 53.9 nm for Ru/rod-CeO₂, Ru/particle-CeO₂ and Ru/cube-CeO₂, respectively. Smaller supports crystallite size is more helpful to disperse Ru. There is only one small peak of Ru (2 Theta = 44 °) observed in the Ru/cube-CeO₂ sample and no observation on Ru/rod-CeO₂ and Ru/particle-CeO₂, indicating that Ru has better dispersion on the rod and particle CeO₂ supports.

The morphologies of the Ru/CeO₂ catalysts were determined using Transmission electron microscopy (TEM). As shown in Fig. 3a and 3b, the Ru/rod-CeO₂ catalyst exhibits a morphology of rod with a uniform diameter (8–10 nm) and length from 20 to 200 nm. Ru/particle-CeO₂ (Fig. 3d and e) and Ru/cube-CeO₂ (Fig. 3g and h) show uniform particle shapes (5–10 nm) and cubic structure (10–50 nm), respectively. The particle size of CeO₂ in various Ru/CeO₂ materials is consistent with the average size calculated from XRD (Table 1). It is noted that all the three CeO₂ supports show a lattice spacing of 0.31 nm, which is assigned to the (1 1 1) lattice plane [30]. The high temperature calcination (600 °C) may induce the uniform crystal lattice. Furthermore, smaller CeO₂ supports particles are suggested to benefit the dispersion of metals, in which the rod-CeO₂ and particle-CeO₂ possess much better Ru dispersion (Fig. 3c, 3f and 3i). The Ru clusters (1–2 nm) on the surface of cube-CeO₂ are much larger, which is consistent with XRD observation (Fig. 2a).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru content (wt.)</th>
<th>CeO₂ (nm)</th>
<th>S₉₅⁰ (m² g⁻¹)</th>
<th>V₉⁰ (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/rod-CeO₂</td>
<td>1.8</td>
<td>9.0</td>
<td>90.2</td>
<td>0.33</td>
</tr>
<tr>
<td>Ru/particle-CeO₂</td>
<td>2.0</td>
<td>6.9</td>
<td>114.0</td>
<td>0.23</td>
</tr>
<tr>
<td>Ru/cube-CeO₂</td>
<td>1.8</td>
<td>53.9</td>
<td>18.0</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* Element percentage evaluated by elemental analysis.
* Average crystallite size obtained from Scherrer’s equation (220 plane at 2 Theta = 47.7 °) was applied to calculate the crystal size.
* Multipoint BET surface area.
* BJH method cumulative desorption pore volume.
Fig. 2. (a) XRD patterns of reduced Ru/CeO$_2$ materials with different CeO$_2$ morphologies; (b) N$_2$ adsorption–desorption isotherms and (c) Pore size distribution of Ru/CeO$_2$ materials (BJH desorption branch).

Fig. 3. TEM images and Ru size distribution of 2 wt% reduced Ru/rod-CeO$_2$ (a, b and c), Ru/particle-CeO$_2$ (d, e and f) and Ru/cube-CeO$_2$ (g, h and i).
3.2. Support-metal interaction and oxygen vacancies of Ru/\(\text{CeO}_2\) materials

To understand the effect of \(\text{CeO}_2\) morphology on supported Ru species, the reducibility of Ru/\(\text{CeO}_2\) materials was investigated using \(\text{H}_2\) temperature-programmed reduction (\(\text{H}_2\)-TPR). As shown in Fig. 4, two distinct peaks are observed at 110–160 °C (peak \(\alpha\)) and 170–190 °C (peak \(\beta\)), which are related to the reduction of RuO\(_x\) species [39]. It is believed that RuO\(_x\) species with reduction peaks at a lower temperature (peak \(\alpha\)) are related to smaller particle size accomplished with Ru-O-Ce bonds [45–46]. In contrast, the bigger RuO\(_x\) clusters, which are composed of Ru-O-Ru bonds [47], needs higher reduction temperature (peak \(\beta\)) [45]. Ru/rod-CeO\(_2\) shows more significant peak \(\beta\) with a lower reduction temperature (118°C) than Ru/particle-CeO\(_2\) (158°C) and Ru/cube-CeO\(_2\) (160°C), indicating more abundant SMI (Ru-O-Ce species). It is noted that all Ru/\(\text{CeO}_2\) materials can be thoroughly reduced before 200°C, indicating the metallic state Ru at ICCM evaluation condition.

The SMI and oxygen vacancies on reducible supports (\(\text{CeO}_2\), \(\text{TiO}_2\), etc.) play key roles in catalytic reactions [43,48]. Therefore, X-ray photoelectron spectrum (XPS) analysis (Fig. 5) was carried out to obtain further insight into the metal states and oxygen vacancies on the Ru/\(\text{CeO}_2\) materials. The valences of Ru are assigned to the peaks of Ru 3\(d_3\) and Ru 3\(d_5\) (Fig. 5a), which are composed of metallic stated Ru\(_0\) (around 280.4 eV and 284.6 eV) and compound stated Ru\(_x\) (around 281.7 eV and 285.8 eV). Ru\(_{2x}\) in Ru/\(\text{CeO}_2\) is attributed to the SMI or Ru diffusion in \(\text{CeO}_2\) lattice [48], and the ratio of Ru\(_{2x}\)/(Ru\(_0\) + Ru\(_{2x}\)) (Table 2) can be used to semi-quantify SMI [49–50]. Ru/rod-CeO\(_2\) shows the highest Ru\(_{2x}\)/(Ru\(_0\) + Ru\(_{2x}\)) suggesting the most abundant SMI and well-dispersed Ru, consistent with \(\text{H}_2\)-TPR results (Fig. 4). Furthermore, an enhanced Ru valence state is believed to facilitate the dissociation of CO\(_2\) into CO [37], which is a pivotal intermediate step of CO\(_2\) methanation.

The peaks of Ce 3d are used to analyze the valence state of Ce (Ce\(^{3+}\) and Ce\(^{4+}\)). Ten peaks constitute two series of spin–orbit lines u and v. Four of the peaks are located at 880.9 eV (v\(_0\)), 884.6 eV (v'), 898.7 eV (u\(_0\)) and 902.7 eV (u'), which belong to Ce\(^{3+}\), while the other six peaks belong to Ce\(^{4+}\) [10]. The presence of Ce\(^{3+}\) is related to oxygen vacancies [39], surface OH groups or carbonate species [43]. As shown in Table 2, the Ru/cube-CeO\(_2\) catalyst has the highest Ce\(^{3+}\)/Ce\(^{4+}\) ratio (0.35), followed by the Ru/particle-CeO\(_2\) (0.28) and Ru/rod-CeO\(_2\) (0.27) catalysts.

The O 1s XPS spectra of Ru/\(\text{CeO}_2\) is shown in Fig. 5c. The peaks at around 529.4 eV and 530.9 eV are assigned to the lattice oxygen (O\(_L\)) and oxygen vacancies (O\(_V\)), respectively [48]. The oxygen vacancies could be ascribed to metal doping [51] or the support materials defects [52]. The ratio of O\(_V\)/O\(_L\) (Table 2) could represent the abundance of oxygen vacancy on \(\text{CeO}_2\). The results show that the Ru/rod-CeO\(_2\) catalyst has the most abundant oxygen vacancy defects compared with the other two catalysts, which is consistent with the analysis of Ce 3d. These oxygen vacancies can promote CO\(_2\) adsorption by forming bicarbonates [53], and might improve the conversion of CO\(_2\) [54].

In summary, Ru/rod-CeO\(_2\) shows the most abundant SMI and highest Ru valence (Fig. 4). On the contrary, Ru/cube-CeO\(_2\) possesses more oxygen vacancies. However, it disperses Ru poorer and has the lowest Ru valence.

3.3. Evaluation of integrated CO\(_2\) capture and methanation (ICCM) on Ru/\(\text{CeO}_2\)-\(\text{MgO}\) combined materials

The ICCM process is a combination of several steps, including CO\(_2\) capture over the physical mixed Li, Na, K-doped MgO (Eq.5), the purge of residual CO\(_2\), and CO\(_2\) methanation accompanied with the regeneration of adsorbs (Eqs. (1) and (6)).

\[
\text{CO}_2 + \text{MgO} \leftrightarrow \text{Mg}_2\text{CO}_3
\]

\[
4\text{H}_2 + \text{Mg}_2\text{CO}_3 = 2\text{MgO} + \text{CH}_4 + 2\text{H}_2\text{O}
\]

The performances of ICCM over Ru/\(\text{CeO}_2\)-\(\text{MgO}\) with different CeO\(_2\) morphologies are shown in Fig. 6. Owing to the partial desorption of CO\(_2\) from the adsorbent, the following analysis focuses on the desorbed one-carbon (C1) species (CO\(_2\) and CH\(_4\)) in the 2nd stage. The desorption capacity of C1 species over combined materials, representing the CO\(_2\) throughput, was evaluated using the sum of CO\(_2\) and CH\(_4\) yield. All the detected C1 species come from the adsorbed CO\(_2\) in the 1st stage of ICCM. The order of C1 species desorption capacity is Ru/particle-CeO\(_2\)-\(\text{MgO}\) (0.49 mmol/g\(_\text{DFM}\)) < Ru/rod-CeO\(_2\)-\(\text{MgO}\) (0.60 mmol/g\(_\text{DFM}\)) < Ru/cube-CeO\(_2\)-\(\text{MgO}\) (1.29 mmol/g\(_\text{DFM}\)), as shown in Fig. 6. Furthermore, there are significant carbonate peaks on the spent combined materials of Ru/cube-CeO\(_2\)-\(\text{MgO}\) (Fig. 7) after releasing the most abundant C1 species, indicating its enhanced CO\(_2\) adsorption compared to the other two materials.

On the contrary, there is no distinguishable peaks of spent Ru/rod-CeO\(_2\)-\(\text{MgO}\) and Ru/particle-CeO\(_2\)-\(\text{MgO}\), representing the sufficient regeneration of MgO after the hydrogenation step. It is speculated that the differences in CO\(_2\) adsorption over the three Ru/\(\text{CeO}_2\)-\(\text{MgO}\) combined materials are related to the different amounts of oxygen vacancies on the surface of CeO\(_2\) with different morphologies. Compared to the rod and particle-CeO\(_2\), the higher oxygen vacancies on the surface of cube-CeO\(_2\) might benefit the formation of bicarbonates [53] to enhance the CO\(_2\) adsorption capacity of combined materials.

However, oxygen vacancies cannot significantly improve the catalytic methanation in ICCM. For example, higher CO\(_2\) conversion was achieved using the combined materials of Ru/rod-CeO\(_2\)-\(\text{MgO}\) (55.7%) and Ru/particle-CeO\(_2\)-\(\text{MgO}\) (59.8%) compared to Ru/cube-CeO\(_2\)-\(\text{MgO}\) (2.7%). It is concluded that better Ru dispersion and SMI promote the catalytic performance of CO\(_2\) utilization. Furthermore, there is no CO generation in ICCM over Ru/\(\text{CeO}_2\)-\(\text{MgO}\) owing to the excellent CH\(_4\) selectivity of Ru. The limited hydrogen spillover from Ru metals to supports might also contribute to high CH\(_4\) selectivity [32].

Several factors contribute to the significantly improved CO\(_2\) conversion and CH\(_4\) yield of Ru/rod-CeO\(_2\)-\(\text{MgO}\) and Ru/particle-CeO\(_2\)-\(\text{MgO}\). (1) The better dispersion of Ru (indicated from TEM analysis, Fig. 3) on rod-CeO\(_2\) and particle-CeO\(_2\) can increase the reactant contact with the Ru active sites. (2) The higher BET surface area could facilitate the accessibility of active sites. (3) The abundant interaction between Ru active metals and CeO\(_2\) supports [17,55] can act as the center of catalytic activities. (4) The abundant oxygen vacancies would lead to the enhanced CO\(_2\) absorption performance. Therefore, it is suggested that the optimal composition of the combined materials with CeO\(_2\) as support is to have abundant SMIs with a well-dispersed active metal site, while

Fig. 4. \(\text{H}_2\)-TPR profiles of Ru/\(\text{CeO}_2\) with different CeO\(_2\) morphologies.
the adjustment of oxygen vacancies is more related to the CO$_2$ capacity in ICCM.

The catalytic stability and reusability of Ru/rod-CeO$_2$-MgO combined materials in ICCM were also investigated in this work. As shown in Fig. 8, it is interesting that the capacity of CO$_2$ desorption decreases from 58.5 to 5.3 μmol/g$_{DFM}$ after 9 cycles, whilst the CH$_4$ yield only decrease ~ 20% (from 0.34 to 0.27 mmol/g$_{DFM}$). Furthermore, the catalytic performance of Ru/rod-CeO$_2$-MgO for ICCM stabilizes after 5 cycles with > 95% CO$_2$ conversion using 5% H$_2$/N$_2$, which outperforms the state-of-the-art conventional CO$_2$ methanation (<70% for CO$_2$ conversion at 300 °C using concentrated CO$_2$ and H$_2$) over Ru-based catalysts [43,56–57].

The mechanism of ICCM over Ru/CeO$_2$-MgO was studied by in situ DRIFTS characterization using Ru/rod-CeO$_2$-MgO catalyst with Ru/rod-CeO$_2$ as the benchmark, as shown in Fig. 9. During the CO$_2$ adsorption of Ru/CeO$_2$-MgO, a set of peaks appeared and gradually increased, including the peaks at 1614 cm$^{-1}$ (bidentate carbonates [58]) and 1815 cm$^{-1}$ (carbonyl vibration of carbonates), which represented the CO$_2$ adsorption on MgO by forming carbonates. The peaks belonging to CO$_2$ adsorption can be saturated within 15 mins over Ru/CeO$_2$-MgO combined materials. As for the key intermediates, we observed CO$_2$ dissociation at the initial time of CO$_2$ adsorption, including the peaks at 2037 cm$^{-1}$ and 1993 cm$^{-1}$ (linear or bridged Ru-CO [14,59–61]).

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru 3d δ/(Ru$^0$ + Ru$^{3+}$)</th>
<th>Ce 3d δ/(Ce$^{3+}$ + Ce$^{4+}$)</th>
<th>O 1s δ/(O$_{2p}$)</th>
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</thead>
<tbody>
<tr>
<td>Ru/rod-CeO$_2$</td>
<td>0.71</td>
<td>0.27</td>
<td>0.18</td>
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<tr>
<td>Ru/particle-CeO$_2$</td>
<td>0.61</td>
<td>0.28</td>
<td>0.20</td>
</tr>
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<td>Ru/cube-CeO$_2$</td>
<td>0.43</td>
<td>0.35</td>
<td>0.30</td>
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</tbody>
</table>
significant peak shift from 1614 cm$^{-1}$ to 1582 cm$^{-1}$ (conjugated C-O/C = O of formats [14,61]) and OCO peak at 1367 cm$^{-1}$ [62], representing the possible formates reaction pathway on the surface of MgCO$_3$. Ru/rod-CeO$_2$ can also adsorb CO$_2$ to form carbonates [63], which may be related to the oxygen vacancies on the surface. In short, there are mainly two reaction pathways in ICCM over Ru/CeO$_2$-MgO, including CO$_2$ dissociation on Ru and formates on MgCO$_3$. The gradually increased CO$_2$ conversion during cyclic ICCM over Ru/rod-CeO$_2$-MgO might be attributed to the promotion of the formates pathway.

Therefore, as illustrated in Fig. 10, it is suggested that (1) in the first step of CO$_2$ adsorption, MgO acts as the main adsorbent to form MgCO$_3$ while CeO$_2$ with oxygen vacancies can promote extra CO$_2$ adsorption by forming bicarbonates. (2) two reaction routes for the release and transformation of the adsorbed CO$_2$ under 5% H$_2$/N$_2$ atmosphere are proposed. Route 1 is the decomposition of MgCO$_3$ to release gas-phase CO$_2$ and then generate CH$_4$ with the assistance of H$_2$ and active sites by the CO$_2$ dissociation pathway. Route 2 is the reduction of carbonates (Eq. (6)) by the formates pathway. Route 2 does not rely on the gas phase CO$_2$ spillover and can achieve ideal ICCM performance, ~100% CO$_2$ conversion.

4. Conclusion

An integrated CO$_2$ capture and methanation (ICCM) process has been performed using Ru/CeO$_2$-MgO combined materials with different CeO$_2$ morphologies, including rod, particle, and cube. In this ICCM process, CO$_2$ adsorption and in situ methanation are isothermally (300 °C) carried out over Ru/CeO$_2$-MgO combined materials in a single reactor. It is demonstrated that there are clear effects of support morphology on CO$_2$ conversion and CH$_4$ yield in ICCM. The results show that Ru/rod-CeO$_2$-MgO and Ru/particle-CeO$_2$-MgO exhibit significantly higher CH$_4$ yield (0.33 and 0.29 mmol/g$_{DFM}$) and CO$_2$ conversion (55.7% and 59.8%) compared with Ru/cube-CeO$_2$-MgO, yielding 0.03 mmol/g$_{DFM}$ CH$_4$ with only 2.7% CO$_2$ conversion. The comprehensive characterizations of combined materials reveal that the rod-CeO$_2$ and particle-CeO$_2$ supported Ru possess higher surface area, better Ru dispersion and more abundant support-metal interactions, contributing to the enhanced ICCM performance. In addition, the oxygen vacancies on CeO$_2$ mainly enhance the CO$_2$ adsorption performance. Notably, the ICCM of Ru/rod-CeO$_2$-MgO shows stable CH$_4$ yield in cycles and can achieve > 95% CO$_2$ conversion after 5 cycles, showing significant superiority compared to traditional CO$_2$ methanation (~70% for CO$_2$ conversion under similar conditions).

The critical intermediates of ICCM were investigated to understand the mechanism of the whole process. In situ DRIFTS study indicates that ICCM over Ru/rod-CeO$_2$-MgO proceeds via the formates and CO$_2$ dissociation (Ru-CO species) pathways. The formates pathway do not require gas phase CO$_2$ to release from carbonates. Therefore, it could contribute to achieving ideal ICCM performance (100% CO$_2$ conversion and 100% CH$_4$ selectivity). Improving the formates pathway and inhibiting gas-phase CO$_2$ release in the methanation step could be a promising strategy to achieve perfect ICCM.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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