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## Highly Durable Ru Catalysts Supported on CeO<sub>2</sub> Nanocomposites for CO<sub>2</sub> Methanation

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**Graphical abstract** 



#### Highlights

- [1] Solvothermally prepared CeO<sub>2</sub>-based materials including CeO<sub>2</sub> aggregates, SiO<sub>2</sub>-CeO<sub>2</sub> nanocomposites, and TiO<sub>2</sub>-CeO<sub>2</sub> nanocomposites were examined as sintering-resistant supports for Ru catalyst in highly exothermic CO<sub>2</sub> methanation.
- [2] High catalytic activity and durability of these prepared Ru catalysts with lowtemperature catalytic activities and constant catalytic performances were demonstrated by heat-cycle test and long-term stability tests.
- [3] Remained good dispersion of small Ru nanoparticles and no enlargement of CeO<sub>2</sub> crystallites of the supports proved the sintering suppression effect of solvothermally prepared CeO<sub>2</sub>-based nanocomposites.

#### Abstract

Taking advantages of the high heat tolerance, large specific surface area, and rough surface morphology created by agglomeration of fine primary particles, a solvothermally prepared CeO<sub>2</sub> aggregate, SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite are proposed to be used as sintering-resistant catalyst supports in highly exothermic reactions. Well-dispersed Ru metal catalysts were deposited on support surfaces by the precipitation–deposition method. The methanation of CO<sub>2</sub> by H<sub>2</sub>, which is a highly exothermic reaction, was selected as a probe reaction in order to evaluate the catalytic activity and sintering-resistant capability of Ru catalysts deposited on those prepared supports. As expected, the low temperature (150–200 °C) activity and CH<sub>4</sub> production of the Ru catalysts on the prepared CeO<sub>2</sub> aggregates. Moreover, long-term stability (400 °C, 24 h; 50–300 °C, 10 cycles) was also achieved in the catalysts on these prepared supports.

**Keywords:** Ru/CeO<sub>2</sub>; Ru/SiO<sub>2</sub>–CeO<sub>2</sub>; Ru/TiO<sub>2</sub>–CeO<sub>2</sub>; sinter-stable supports; CeO<sub>2</sub> composites; CO<sub>2</sub> methanation.

#### 1. Introduction

The suppression of thermal sintering of metal nanoparticles and the thermal deformation of catalyst supports in supported catalysts are critical issues in practice, especially when catalysts are applied to high temperature catalytic processes [1–3]. In general, nanosized metal particles and their supports tend to migrate under severe reaction conditions, such as high temperature, generating enlarged agglomerates with a morphological change as well as losing their surface area and catalytic activity [4–7].

Therefore, it is crucial to retain the original size and morphology of both metal nanoparticles and catalyst supports. Several anti-sintering strategies in both chemical and physical approaches, for example, alloying, ligand-assisted pinning, encapsulation (e.g., core shell and core sheath), and fixing metal nanoparticles on defects of catalyst supports, have been investigated [8–14]. These strategies, however, are still in progress.

Recently, we developed a versatile and facile one-pot/single-step solvothermal approach to fabricate metal oxide nanoparticle assemblies such as SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub> with submicron-sized special morphologies, named micro/mesoporously architected roundly integrated oxide (MARIMO) [15–17]. MARIMO metal nanocomposites consisting of several metal oxides are also easily obtained by the solvothermal approach. The obtained MARIMO assemblies consist of an ultrafine nanoconcave-convex surface with a huge surface area. For example, the TiO<sub>2</sub> MARIMO assembly consists of numerous primary nanoparticles with ca. 5 nm diameter, and the specific surface area exceeds 200 m<sup>2</sup>/g and reaches 400 m<sup>2</sup>/g. Therefore, the TiO<sub>2</sub> MARIMO assembly with its large specific surface area and nano-concave-convex surface structure is expected to be an excellent support for catalyst metal nanoparticles, because the nano-concave-convex surface structure can disperse metal nanoparticles well and prevent metal nanoparticles from migrating to aggregates. Indeed, the use of the TiO<sub>2</sub> MARIMO assembly as a catalyst support successfully enhanced the dispersion of Au nanoparticles on the surface and suppressed the sintering of Au nanoparticles during highly exothermic CO oxidation [18]. However, the heat tolerance of the  $TiO_2$ support turned out to be insufficient in this reaction, and the support gradually started to be sintered, which impelled us to study better supports with higher heat tolerance.

Among metal oxides utilized for catalytic applications, CeO<sub>2</sub> is an attractive material because of its high and unique catalytic activity derived from the Ce<sup>3+</sup>/Ce<sup>4+</sup> redox change [19–26]. Additionally, a possible strong interaction between CeO<sub>2</sub> and metal nanoparticles such as Ru, Pd, and Pt would enhance metal dispersion, catalytic

efficiency, and suppression of migration of active metal nanoparticles [27–33]. Moreover, the properties of CeO<sub>2</sub> can be tuned or enhanced by mixing with other metal oxides at a nano-level to yield CeO<sub>2</sub> nanocomposites. Actually, we reported that the SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites with a 1:1 Si/Ce mole ratio exhibited a large specific surface area exceeding 300 m<sup>2</sup>/g, as well as excellent heat tolerance with almost no serious damage under heating at either 700 °C for 24 h or 850 °C for 3 h, compared to monocomponent CeO<sub>2</sub> [34]. With these advantages, CeO<sub>2</sub> assemblies and CeO<sub>2</sub> nanocomposites with ultrafine surface roughness, which are synthesized by our original solvothermal synthesis method, are highly expected to be effective and sintering-resistant catalyst supports, especially when the reaction is performed at an elevated temperature.

Herein, we report the heat tolerance of newly prepared CeO<sub>2</sub>-based materials, as sintering-resistant supports, including CeO<sub>2</sub> assemblies, SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites. Methanation of CO<sub>2</sub> by H<sub>2</sub> catalyzed by Ru, which is one of the most important reactions for  $CO_2$  recycling [35–37], was selected as a probe reaction to estimate sintering resistance of the catalysts, since the reaction is known as a highly exothermic reaction ( $\Delta H_{298K}$  = -165 kJ/mol). When the methanation is performed in a small scale, temperature control of the catalyst bed is relatively easy because of small amount of generated reaction heat from the exothermic reaction. However, in the case of large scale reaction, such as bench-top scale or more, total amount of the reaction heat is quite much. In this case, temperature control of the catalyst bed becomes seriously important. If the methanation reaction meet "runaway (out of control)" accidentally, the catalysts will be exposed to high temperature, which surely leads to sintering of the catalyst Ru nanoparticles. Once sintering of the Ru nanoparticles occurs, catalytic activity will be lost and no recovery can be expected even after the catalyst bed temperature is lowered. In order to avoid such catastrophic situation, the reactant gases are sometimes diluted by inert gas or the reactor is cooled from the outside not to reach such high temperature, which need more cost practically. Then, if the catalysts for the

exothermic reactions could tolerate such accidental and/or unexpected temperature jump, it would be very meaningful to realize sintering-resistant catalytic systems. Thus, for exothermic CO<sub>2</sub> methanation, sintering suppression of the supported metal nanoparticle catalyst under unexpected high temperature conditions is extremely important in order to keep the catalysts stable.

#### 2. Experimental Section

#### 2.1. Materials

Methanol, cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), tetraethyl orthosilicate (Si(OEt)<sub>4</sub>), titanium tetraisopropoxide (Ti(O<sup>*i*</sup>Pr)<sub>4</sub>), sodium hydroxide (NaOH), ruthenium chloride trihydrate (RuCl<sub>3</sub>·3H<sub>2</sub>O), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine ((CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, TMEDA), commercial cerium oxide (commercial CeO<sub>2</sub>), and washed sea sand (425~850 µm) were purchased from FUJIFILM Wako Pure Chemical Corporation. All chemicals were used as received without further purification.

# 2.2. Preparation of the CeO<sub>2</sub> Assembly, SiO<sub>2</sub>–CeO<sub>2</sub> Nanocomposite, and TiO<sub>2</sub>–CeO<sub>2</sub> Nanocomposite

Synthesis of the CeO<sub>2</sub> assembly and SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite was carried out by the solvothermal reaction of a precursor solution including Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mol/L), Si(OEt)<sub>4</sub> (0.1 mol/L), and TMEDA (0.2 mol/L) in methanol (3.5 mL) at 300 °C according to a similar procedure described previously [34]. The TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite with a 1:1 molar ratio of Ti/Ce was prepared by a similar procedure using Ti(O<sup>*i*</sup>Pr)<sub>4</sub> instead of Si(OEt)<sub>4</sub>.

#### 2.3. Preparation of Ru Catalysts

Supported Ru catalysts were prepared by the precipitation-deposition method with an intended Ru amount of 3 wt%. The powdery support (1 g, commercially available and

solvothermally prepared) was dispersed in 27 mL of reverse osmosis water prior to the addition of 80 mg of RuCl<sub>3</sub>·3H<sub>2</sub>O. NaOH solution (0.1 mol/L) was added slowly to the suspension with vigorous stirring to adjust the pH to 8.0~8.5. The mixture was vigorously stirred for another 3 h, and then the mixture was centrifuged. The obtained precipitate was collected and washed three times with water and dried at 60 °C for 12 h in an oven. The obtained powdery product was reduced in a mixed gas stream of H<sub>2</sub> and N<sub>2</sub> (40% H<sub>2</sub> and 60% N<sub>2</sub>) at 200 °C for 3 h. The obtained 3 wt% Ru catalysts supported on the commercial CeO<sub>2</sub> assembly, solvothermally prepared CeO<sub>2</sub> assembly, solvothermally prepared TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite, and solvothermally prepared TiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, respectively.

#### 2.4. Characterization

Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100F microscope. High-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on an Oxford INCA X-Max 80 EDX spectrometer with the above TEM instrument. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was measured on a Hitachi High-Tech Science PS3520UV-DD spectrometer. Nitrogen (N<sub>2</sub>) adsorption/desorption experiments were conducted on a MicrotracBEL BELSORP-mini II. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method through obtained N<sub>2</sub> adsorption–desorption isotherms. The crystalline phases of the resultant nanoparticle nanocomposites were identified by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer using graphite-monochromated Cu Kα radiation. Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed at BL15XU of SPring-8. The excitation photon energy was fixed to 5.95 keV, and the total energy resolution was set to 240 meV.

The reducibility of these prepared catalysts was studied by temperature-programmed reduction of hydrogen (H<sub>2</sub>-TPR) with a flow-type reactor (BELCAT II; MicrotracBEL). The catalysts (50 mg) were pretreated in a mixed gas flow of O<sub>2</sub>/Ar (20% O<sub>2</sub> and 80% Ar) at 300 °C for 30 min prior to H<sub>2</sub>-TPR. The H<sub>2</sub>-TPR experiment was executed in a temperature range of 40–900 °C, with a ramping rate of 10 °C/min, in a mixed gas of 6% H<sub>2</sub> in Ar.

Pulsed chemisorption using CO gas (CO chemisorption) was carried out to characterize the Ru active sites of the catalysts. 100 mg of the catalysts was pretreated by  $H_2$  at 120 °C for 15 min prior to CO adsorption with a mixed stream of 5% CO in He at room temperature.

#### 2.5. Evaluation of Catalytic Activity

The catalytic activity of the Ru catalysts for CO<sub>2</sub> methanation was tested using the flow-type reactor (BELCAT II; MicrotracBEL). Before performing the reaction, the catalyst sample (100 mg) diluted by the washed sea sand (100 mg) was packed into the reactor and then pretreated under a H<sub>2</sub> stream at 120 °C for 15 min. Then, CO<sub>2</sub> methanation was conducted by feeding an inlet gas stream of CO<sub>2</sub>/H<sub>2</sub>/Ar (5% CO<sub>2</sub>, 20% H<sub>2</sub>, and 75% Ar) at a total flow rate of 20 mL/min. The outlet gases were analyzed by a gas chromatograph (GC3200; GL Sciences) using a thermal conductivity detector.

The stability and durability of the catalysts against sintering were evaluated through three different experiments: three-run test, 10-cycle test, and long-term stability test. In these catalytic tests, the reaction processes were sequentially repeated several times or constantly kept under high temperature conditions. For the three-run test, the whole  $CO_2$  methanation process in a temperature range of 150–600 °C was sequentially repeated three times. The temperature step and the reaction time at each temperature were kept at 50 °C and for 30 min, respectively. The 10-cycle test was carried out by repeating  $CO_2$  methanation 10 times at a low temperature of 50 °C and a high temperature of 300 °C

alternately. In each cycle of the 10-cycle test, the reaction time was kept at 30 min at each temperature. The long-term stability test was performed over a period of 24 h at a constant temperature of 400 °C. In the cases of the three-run test and the 10 cycle test, 100 mg of catalysts were used, while 25 mg of catalysts were used in the long-term stability test in expectation of earlier activity loss of the catalysts.

#### 3. Results and Discussion

#### 3.1. Properties of Ru Catalysts Supported on CeO<sub>2</sub>-Based Materials

Due to the fact that the large specific surface area and excellent heat tolerance of catalyst supports are quite suitable for good dispersion and stabilization of catalyst metals, our reported  $SiO_2$ –CeO<sub>2</sub> nanocomposites are potential supports to suppress the sintering of catalyst metals. We also selected the TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite as a different type of support here, because some interactions between catalyst metals and TiO<sub>2</sub> supports can be expected [38,39].

Dispersion of metal nanoparticles on supports is an essential factor that directly influences the catalytic activity in supported catalysts. The properties of the as-prepared catalysts were investigated using TEM, HAADF-STEM, EDX, CO chemisorption, XRD, and HAXPES measurements (Table 1, Figure 1, and Figures S1–S5). The TEM observations and CO chemisorption of the as-prepared catalysts reveal that the Ru particle size on commercial CeO<sub>2</sub> (Ru/commercial CeO<sub>2</sub>) was quite large (7.7 nm by TEM) as compared to those of Ru on the prepared CeO<sub>2</sub> (Ru/CeO<sub>2</sub>), the SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite (Ru/SiO<sub>2</sub>–CeO<sub>2</sub>), and the TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite (Ru/TiO<sub>2</sub>–CeO<sub>2</sub>) (Figure 1). In the case of Ru/CeO<sub>2</sub>, the Ru nanoparticles were too small to be recognized in the TEM image. In the cases of Ru/SiO<sub>2</sub>–CeO<sub>2</sub> and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, the average Ru nanoparticle sizes were measured to be so small, 0.6 and 1.0 nm, respectively.

The average crystallite sizes of  $CeO_2$  in  $Ru/CeO_2$  (6.1 nm, Scherrer equation),  $Ru/SiO_2$ -CeO<sub>2</sub> (1.7 nm), and  $Ru/TiO_2$ -CeO<sub>2</sub> (2.2 nm) are much smaller than that in

Ru/commercial CeO<sub>2</sub> (49 nm), resulting in a much larger specific surface area of Ru/CeO<sub>2</sub> (93 m<sup>2</sup>/g), Ru/SiO<sub>2</sub>–CeO<sub>2</sub> (180 m<sup>2</sup>/g), and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> (177 m<sup>2</sup>/g) than that of Ru/commercial CeO<sub>2</sub> (4.0 m<sup>2</sup>/g). In addition, the Ru dispersivity of Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> determined by CO pulse experiment is much better than that of Ru/commercial CeO<sub>2</sub>. Homogeneous distribution of Ru nanoparticles was also confirmed by STEM/EDX measurement of the supported Ru catalysts. The Ru contents quantified by ICP-OES analysis were 3.7, 3.4, 3.0, and 2.9 wt% for Ru/commercial CeO<sub>2</sub>, Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, respectively. These results are consistent with Ru contents from STEM-EDX analysis (Table 1). Thus, the Ru nanoparticle and CeO<sub>2</sub> crystallite sizes of the prepared Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> are much smaller than those of Ru/commercial CeO<sub>2</sub>.

Next, the XRD patterns of the prepared catalysts Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> showed only reflection peaks ascribed to cubic CeO<sub>2</sub>, whereas no peaks derived from Ru, SiO<sub>2</sub>, and/or TiO<sub>2</sub> were detected (Figure S4), indicating that SiO<sub>2</sub> and TiO<sub>2</sub> in the nanocomposites existed in amorphous phases. The existence of Ru on the CeO<sub>2</sub> and SiO<sub>2</sub>–CeO<sub>2</sub> supports was also confirmed by HAXPES measurements (Figure S5).

The H<sub>2</sub>-TPR experiments were performed in order to clarify the surface properties of the catalyst supports and Ru nanoparticles on the supports (Figure 2). As a result, three types of responses were mainly observed for the prepared Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> (Figures 2b–2d), whereas two responses were found for Ru/commercial CeO<sub>2</sub> (Figure 2a). The peak that appeared at 100–200 °C can be attributed to the reduction of ruthenium oxides [40,41]. The peaks at 250–350 °C and around 800 °C can be ascribed to the reduction of the surface and the bulk of CeO<sub>2</sub>, respectively [27,42–44]. In addition, a peak was observed at 550–600 °C only in the case of Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, which can be assigned to the reduction of TiO<sub>2</sub> [45]. Therefore, the surface oxidation states of the prepared Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>

are different from that of Ru/commercial CeO<sub>2</sub>. Moreover, in the case of the prepared Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, the reduction of Ru species around 100– 200 °C initiated at a lower temperature range, suggesting the existence of some interactions between Ru and the supports favorable to H<sub>2</sub> reduction. Notably, H<sub>2</sub> uptakes of 2.90 mmol/g for Ru/SiO<sub>2</sub>–CeO<sub>2</sub> and 1.99 mmol/g for Ru/TiO<sub>2</sub>–CeO<sub>2</sub> at below 250°C were considerably higher than those of the Ru catalysts on the monocomponent CeO<sub>2</sub>, which would indicate their greater reduction of Ru species (Table S1). Moreover, those values remarkably exceeded the theoretically required H<sub>2</sub> amount of 0.59 mmol/g to convert RuO<sub>2</sub> to metallic Ru, suggesting that a partial reduction of the composite supports are included.

# 3.2. Catalytic activity and durability of Ru catalysts supported on CeO<sub>2</sub>-Based Materials

The prevention of sintering is an important requirement for catalysts to achieve a long lifetime. Here highly exothermic  $CO_2$  methanation was selected as a probe reaction in order to check the sintering resistance of the catalysts. The catalytic activity and durability of the prepared catalysts were studied by a three-run experiment in a temperature range of 150–600 °C. The obtained CH<sub>4</sub> yields in the range of 100–400 °C are given in Figure 3. The detailed CO<sub>2</sub> consumption, CH<sub>4</sub> yield, and CO formation over the catalysts are shown in Figure S6.

When Ru/commercial CeO<sub>2</sub> was used as a catalyst, the maximum CH<sub>4</sub> yield was achieved at 350 °C to reach 55% (Figure 3a). However, when the prepared Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> catalysts were used, higher yields of ca. 80% were obtained (Figures 3b–3d). The biggest advantage of our composite catalysts was seen in repeated reactions. When the reaction was repeated twice in the case of Ru/commercial CeO<sub>2</sub>, the CH<sub>4</sub> yield profile drastically shifted to a higher temperature; namely, the catalytic activity clearly decreased (Figure 3a). On the contrary, almost no

deactivation was observed in the prepared Ru/CeO<sub>2</sub> even after the third run of the reaction (Figure 3b). Interestingly, the low temperature activity at 150–200 °C was obviously improved in the cases of Ru/SiO<sub>2</sub>–CeO<sub>2</sub> and Ru/TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites when the reactions were repeated (Figures 3c and 3d). It is difficult to put forward a conclusive discussion. However, this could be ascribed to the enhanced interactions between the support nanoparticles and the Ru metal particles under high temperature conditions. A similar positive effect of heating on the catalytic activity of supports was reported for calcined Ru/CeO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts with strengthened interactions between Ru and ceria supports as well as between Ru and titania supports [32,46,47].

In order to clarify the sintered structure of both metal particles and supports, the morphological changes of the catalysts after the three-run test were directly investigated by TEM and HAADF-STEM observations (Figure 4), and the estimated Ru mean diameters are listed in Table 1.

Figure 4a shows the existence of large-sized Ru nanoparticles deposited on the commercial CeO<sub>2</sub> support, whose particle size changed from 7.7 to 9.6 nm (Table 1). However, the existence of a small amount of much larger Ru nanoparticles (20–30 nm) was confirmed (Figure 5a), indicating that the conditions of the three-run test were so severe for the Ru/commercial CeO<sub>2</sub> catalyst to cause sintering. In contrast, uniform Ru dispersions on CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> were retained after the three-run test, as demonstrated by HAADF-STEM images and EDX mappings, where no Ru agglomerations were observed (Figures 4b–4d). The growth of only small Ru nanoparticles was observed in the cases of Ru/SiO<sub>2</sub>–CeO<sub>2</sub> and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>, and the particle size still remained 1–2 nm (Table 1, Figures 5b and 5c). Interestingly, no enlargement of the CeO<sub>2</sub> crystallites was observed even after the three-run test (Table 1), revealing the effective sintering suppression of Ru nanoparticles as well as CeO<sub>2</sub> crystallites on/in both SiO<sub>2</sub>–CeO<sub>2</sub> and TiO<sub>2</sub>–CeO<sub>2</sub> supports, where the introduced amorphous SiO<sub>2</sub> and TiO<sub>2</sub> in the supports could suppress the crystal growth of CeO<sub>2</sub>

nanoparticles. These discussed results indicate that remained good dispersion of Ru nanoparticles on the prepared CeO<sub>2</sub>-based supports during CO<sub>2</sub> methanation could be a reason for maintained activity of the catalysts.

As a result, the Ru/TiO<sub>2</sub>-CeO<sub>2</sub> nanocomposite exhibited the best performance of not only the low temperature activity and the maximum yield, but also the sintering resistance of Ru nanoparticles and  $CeO_2$  crystallite in  $CO_2$  methanation. As presented in Figure 6, the Ce3d HAXPES spectra of the supports showed Ce3+/Ce4+ coexistence in the prepared CeO<sub>2</sub> composite supports, whereas only the Ce<sup>4+</sup> oxidation state was formed in the case of the commercial CeO<sub>2</sub>. The peak positions of Ce<sup>4+</sup> and Ce<sup>3+</sup> marked by yellow and green in Figure 6, respectively, were obtained from the literatures [38,48]. Moreover, it is noted that the  $TiO_2$ –CeO<sub>2</sub> composite exhibited a favored Ce<sup>3+</sup> formation that could be responsible for its higher catalytic activity as compared to the prepared monocomponent CeO<sub>2</sub>. These results agree well with the previous literature where the Ce-Ti interface was reported to strongly promote the Ce<sup>3+</sup> existence because of the electron contact [38]. It is reported that Ce<sup>3+</sup> sites created on the CeO<sub>2</sub> surface are involved in activation of CO<sub>2</sub>, contributing to a better activity of catalysts [19,27,49,50]. Indeed, Ce<sup>3+</sup> sites act as active sites for adsorption and dissociation of CO<sub>2</sub> to form carbonaceous intermediates which are rapidly hydrogenated into CH<sub>4</sub> molecules. Therefore, the abundant Ce<sup>3+</sup> formation on the surface of the CeO<sub>2</sub>-based catalysts is advantage in promoting CO<sub>2</sub> methanation. Thus, the prepared CeO<sub>2</sub>, SiO<sub>2</sub>-CeO<sub>2</sub>, and TiO<sub>2</sub>-CeO<sub>2</sub> nanocomposites turned out to be promising sintering-resistant catalyst supports for the elevated temperature process of CO<sub>2</sub> methanation.

#### Calcined Catalysts

According to the above-mentioned activity enhancement of Ru catalysts supported on CeO<sub>2</sub>-based materials after the three-run test, CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> were calcined at 500 °C for 2 h prior to Ru deposition in the expectation of catalytic

activity enhancement, yielding Ru/calcined CeO<sub>2</sub>, Ru/calcined SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/calcined TiO<sub>2</sub>–CeO<sub>2</sub>, respectively. The crystallite sizes of CeO<sub>2</sub> in Ru/CeO<sub>2</sub>, Ru/calcined SiO<sub>2</sub>–CeO<sub>2</sub>, and Ru/calcined TiO<sub>2</sub>–CeO<sub>2</sub> (Table 2) are quite comparable to those after the three-run test (Table 1). The specific surface areas of the calcined catalysts are a little bit larger than those after the three-run test. When the calcined catalysts were used for CO<sub>2</sub> methanation, Ru/calcined CeO<sub>2</sub> and Ru/calcined TiO<sub>2</sub>–CeO<sub>2</sub> (Figure 7). The low-temperature catalytic activity of Ru/calcined CeO<sub>2</sub> (150–250 °C) towards CO<sub>2</sub> methanation in the present study is comparable with those in the literatures [19,27]. Notably, an obvious enhancement of low temperature activity at 150–200 °C was observed in the case of Ru/calcined TiO<sub>2</sub>–CeO<sub>2</sub>.

#### 3.3. Long-Term Stability Test of the Ru Catalysts

As mentioned in the former section, the prepared CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> supports led to a high activity and high sintering resistance for Ru catalysts as compared to the commercial CeO<sub>2</sub> support. In order to further support the aforementioned discussions, the stability and durability of the catalysts were investigated through two different experiments: a <u>10-cycle test</u> and a <u>long-term experiment</u>. In the 10-cycle test, severe heat stress was placed on the catalysts, where CO<sub>2</sub> methanation was repeated 10 times at a low temperature (50 °C) and a high temperature (300 °C) alternatively. In each cycle, the reaction time was 30 min at each reaction temperature. Figure 8a clearly shows stable CH<sub>4</sub> production over Ru/CeO<sub>2</sub> during the 10-cycle experiment. Likewise, a stable catalytic performance with almost no change in the CH<sub>4</sub> yield between the 1st and the 10th cycles was observed when the Ru/TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite was used (Figure 8c). However, under similar conditions, the catalytic performance over Ru/commercial CeO<sub>2</sub> decreased gradually by each cycle, clearly indicating catalytic activity loss by thermal sintering (Figure S7). In addition, the long-term stability of Ru/CeO<sub>2</sub> was

confirmed by a constant CH<sub>4</sub> yield as the time-on-stream increased to 24 h (Figures 8b and 8d) at 400 °C. In contrast, the long-term stability test for 24 h at 400 °C with the use of Ru/commercial CeO<sub>2</sub> catalyst resulted in 2% initial yield of CH<sub>4</sub>, but the yield reduced gradually to 0% within 10 h. Thus, the three prepared CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites were effective supports in enhancing the catalyst activity and durability of Ru catalysts for CO<sub>2</sub> methanation. Their further applications in other high temperature systems are highly expected.

#### 4. Conclusions

A porous CeO<sub>2</sub> aggregate, SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite, all of which consisted of numerous amounts of small primary particles (<5 nm) with a huge surface area, were solvothermally prepared as catalyst supports for highly exothermic reactions. Ru nanoparticles were deposited on the support surface by the precipitation–deposition method. The prepared catalyst supports of CeO<sub>2</sub> aggregate, SiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposite dispersed Ru nanoparticles very well on the surface. When they were used as catalysts for CO<sub>2</sub> methanation by H<sub>2</sub>, the Ru catalysts on the prepared CeO<sub>2</sub> aggregate and TiO<sub>2</sub>–CeO<sub>2</sub> exhibited a better low temperature (150–200 °C) activity and long-term stability (400 °C, 24 h) than those on the commercial CeO<sub>2</sub> aggregate. Thus, we succeeded in preparing sintering-resistant catalyst supports for high temperature reactions.

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#### References

- [1] E. D. Goodman, J. A. Schwalbe, M. Cargnello, ACS Catal. 7 (2017) 7156-7173.
- [2] T. W. Hansen, A. T. Delariva, S. R. Challa, A. K. Datye, Acc. Chem. Res. 46 (2013) 1720–1730.
- [3] G. Busca, in: Heterogeneous Catalytic Materials Solid State Chemistry, Surface Chemistry and Catalytic Behaviour, Chapter 4, Elsevier, Oxford, 2014, pp. 37–55.
- [4] E. Bayram, J. Lu, C. Aydin, N. D. Browning, S. Ozkar, E. Finney, B. C. Gates, R. G. Finke, ACS Catal. 5 (2015) 3514–3527.
- [5] Q. Xu, K. C. Kharas, B. J. Croley, A. K. Datye, ChemCatChem 3 (2011), 1004–1014.
- [6] C. H. Bartholomew, Appl. Catal., A 212 (2001) 17-60.
- [7] Ali M. Abdel-Mageed, D. Widmann, S. E. Olesen, I. Chorkendorf, R. J. Behm, ACS Catal. 8 (2018) 5399–5414.
- [8] J. Im, M. Choi, ACS Catal. 6 (2016) 2819-2826.
- [9] B. Mutz, M. Belimov, W. Wang, P. Sprenger, M. Serrer, D. Wang, P. Pfeifer, W. Kleist, J. Grunwaldt, ACS Catal. 7 (2017) 6802–6814.
- [10] L. Adijanto, D. A. Bennett, C. Chen, A. S. Yu, M. Cargnello, P. Fornasiero, R. J. Gorte, J. M. Vohs, Nano Lett. 13 (2013) 2252–2257.
- [11] P. M. Arnal, M. Comotti, F. Schuth, Angew. Chem. Int. Ed. 45 (2006), 8224-8227.

- [12] S. Lee, J. Seo, W. Jung, Nanoscale 8 (2016) 10219-10228.
- [13] G. Prieto, J. Zecevic, H. Friedrich, K. P. d. Jong, P. E. Jongh, Nat. Mater. 12 (2013) 34–39.
- [14] K. Yoon, Y. Yang, P. Lu, D. Wan, H.C. Peng, K. S. Masias, P. T. Fanson, C. T. Campbell, Y. Xia, Angew. Chem. Int. Ed. 51 (2012) 9543–9546.
- [15] P. Wang, K. Ueno, H. Takigawa, K. Kobiro, J. Supercrit. Fluids 78 (2013), 124–131.
- [16] P. Wang, K. Kobiro, Pure Appl. Chem. 86 (2014) 785–800.
- [17] E. K. C. Pradeep, T. Habu, H. Tooriyama, M. Ohtani, K. Kobiro, J. Supercrit. Fluids 97 (2015) 217–223.
- [18] F. Duriyasart, A. Irizawa, K. Hayashi, M. Ohtani, K. Kobiro, ChemCatChem 10 (2018) 3392–3396.
- [19] F. Wang, S. He, H. Chen, B. Wang, L. Zheng, D. G. Evans, X. Duan, J. Am. Chem. Soc. 138 (2016) 6298–6305.
- [20] F. Wang, C. Li, X. Zhang, M. Wei, D. G. Evans, X. Duan, J. Catal. 329 (2015) 177–186.
- [21] S. P. P. Dutta, M. S. Seehra, Y. Shi, E. M. Eyring, R. D. Ernst, Chem. Mater. 18 (2006) 5144–5146.
- [22] E. Aneggi, D. Wiater, C. Leitenburg, J. Llorca, A. Trovarelli, ACS Catal. 4 (2014) 172–181.
- [23] J. Li, G. Lu, G. Wu, D. Mao, Y. Wang, Y. Guo, Catal. Sci. Technol. 2 (2012) 1865–1871.
- [24] J. Li, Z. Zhang, W. Gao, S. Zhang, Y. Ma, Y. Qu, ACS Appl. Mater. Interfaces 8 (2016)22988–22996.
- [25] Y. Li, Q. Sun, M. Kong, W. Shi, J. Huang, J. Tang, X. Zhao, J. Phys. Chem. C 115 (2011) 14050–14057.
- [26] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, Chem. Rev. 116 (2016) 5987–6041.

- [27] Y. Guo, S. Mei, K. Yuan, D. J. Wang, H. Liu, C. H. Yan, Y. W. Zhang, ACS Catal. 8 (2018) 6203–6215.
- [28] P. Concepcion, A. Corma, J. Silvestre-Albero, V. Franco, J. Y. Chane-Ching, J. Am. Chem. Soc. 126 (2004) 5523–5532.
- [29] S. Gatla, D. Aubert, G. Agostini, O. Mathon, S. Pascarelli, T. Lunkenbein, M. G. Willinger, H. Kaper, ACS Catal. 6 (2016) 6151–6155.
- [30] P. G. Lustemberg, P. J. Ramírez, Z. Liu, R. A. Gutiérrez, D. G. Grinter, J. Carrasco,
  S. D. Senanayake, J. A. Rodriguez, M. V. Ganduglia Pirovano, ACS Catal. 6 (2016) 8184–8191.
- [31] M. Tamura, T. Kitanaka, Y. Nakagawa, K. Tomishige, ACS Catal. 6 (2016), 376–380.
- [32] S. Hosokawa, M. Taniguchi, K. Utani, H. Kanai, S. Imamura, Appl. Catal., A 289 (2005) 115–120.
- [33] K. R. Priolkar, P. Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, N. P. Lalla, Chem. Mater. 14 (2002) 2120–2128.
- [34] H. T. T. Nguyen, M. Ohtani, K. Kobiro, Microporous Mesoporous Mater. 273 (2019) 35–40.
- [35] J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, RSC Adv. 5 (2015) 22759-22776.
- [36] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, Fuel 166 (2016) 276–296.
- [37] J. Gao, J. Wang, Y. Ping, D. Hu, G. Xu, F. Gu, F. Su, RSC Adv. 2 (2012) 2358-2368.
- [38] M. J. Muñoz-Batista, M. N. Gomez Cerezo, A. Kubacka, D. Tudela, M. Fernandez García, ACS Catal. 4 (2014) 63–72.
- [39] A. M. Abdel-Mageed, D. Widmann, S. E. Olesen, I. Chorkendorff, J. Biskupek, R. J. Behm, ACS Catal. 5 (2015) 6753–6763.
- [40] X. Liao, K. Li, X. Xiang, S. G. Wang, X. She, Y. Zhu, Y. Li, J. Ind. Eng. Chem. 18 (2012) 818–821.

- [41] N. Hamzah, N. M. Nordinc, A. H. A. Nadzri, Y. A. Nik, M. B. Kassim, M. A. Yarmo, Appl. Catal., A 419–420 (2012), 133–141.
- [42] J. Okal, M. Zawadzki, P. Kraszkiewicz, K. Adamska, Appl. Catal., A 549 (2018) 549, 161–169.
- [43] Z. Hu, X. Liu, D. Meng, Y. Guo, Y. Guo, G. Lu, ACS Catal. 6 (2016) 2265-2279.
- [44] Z. Ma, S. Zhao, X. Pei, X. Xiong, B. Hu, Catal. Sci. Technol. 7 (2017), 191-199.
- [45] H. Zhu, Z. Qin, W. Shan, W. Shen, J. Wang, J. Catal. 7 (2004) 267-277.
- [46] S. Hosokawa, H. Kanai, K. Utani, Y. Taniguchi, Y. Saito, S. Imamura, Appl. Catal., B 45 (2003) 181–187.
- [47] A. Kim, D. P. Debecker, F. Devred, V. Dubois, C. Sanchez, C. Sassoye, Appl. Catal., B 220 (2018) 615–625.
- [48] C. Barth, C. Laffon, R. Olbrich, A. Ranguis, P. Parent, M. Reichling, Sci. Rep. 6 (2016) 21165–21171.
- [49] C. Leitenburg, A. Trovarelli, J. Kaspar, J. Catal. 166 (1997) 98-107.
- [50] P. A. Ussa Aldana, F. Ocampo, K. Kobl, B. Louis, F. Thibault-Starzyk, M. Daturi, P. Bazin, S. Thomas, A.C. Roger, Catal. Today 215 (2013) 201–207.

Table 1. Properties of CeO<sub>2</sub> assemblies and CeO<sub>2</sub> nanocomposites supported Ru catalysts.

		Ru particle size (nm)		Ru dispersivitv <sup>c</sup>	Ru content (wt%)		CeO <sub>2</sub>	Specific
Sample <sup>a</sup>	-	From TEM <sup>b</sup>	From CO chemisorption <sup>c</sup>	(%)	From ICP <sup>d</sup>	From EDX <sup>e</sup>	crystallite size <sup>f</sup> (nm)	surface area <sup>g</sup> (m²/g)
As-prepared	Ru/commercial CeO2	7.7 ± 3.2	15.0	9.0	3.7	1.2	49	4.0
	Ru/CeO <sub>2</sub>	h	1.6	83.4	3.4	4.2	6.1	93
	Ru/SiO <sub>2</sub> –CeO <sub>2</sub>	0.6 ± 0.3	2.6	52.3	3.0	4.0	1.7	180
	Ru/TiO <sub>2</sub> –CeO <sub>2</sub>	1.0 ± 0.2	1.6	81.2	2.9	3.1	2.2	177
After a three- run test	Ru/commercial CeO2	9.6 ± 4.8	—	_	4.0	1.9	48.7	3.9
	Ru/CeO <sub>2</sub>	<u>g</u>	_	_	3.3	4.2	10.3	39.6
	Ru/SiO <sub>2</sub> -CeO <sub>2</sub>	1.2 ± 0.4	_	_	3.1	4.5	1.7	61.1
	Ru/TiO2–CeO2	1.4 ± 0.3	_	_	2.4	3.2	2.1	68.3

<sup>a</sup> The Ru catalysts (3 wt%) deposited on commercial CeO<sub>2</sub>, prepared CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> supports.

<sup>b</sup> Estimated by TEM images from at least 50 Ru particles.

<sup>c</sup>Calculated from CO adsorption measurements.

<sup>d</sup> Quantified by ICP-OES measurement.

<sup>e</sup> Quantified by STEM/EDX analysis on TEM.

<sup>f</sup> The Scherrer equation was used.

<sup>g</sup> The BET method was used. <sup>h</sup> Too small to be estimated by TEM.

Sample <sup>a</sup>	CeO <sub>2</sub> crystallite size <sup>b</sup> (nm)	Specific (m²/g)	surface	area <sup>c</sup>	
Ru/calcined CeO <sub>2</sub>	8.9	63.5			
Ru/calcined SiO <sub>2</sub> -CeO <sub>2</sub>	2.6	120			
Ru/calcined TiO2-CeO2	2.3	119			

**Table 2.** CeO<sub>2</sub> crystallite size and specific surface area of the Ru catalysts prepared on the different calcined supports.

<sup>a</sup> The Ru catalysts (3 wt%) deposited on the supports calcined at 500 °C for 2 h.

<sup>b</sup> Estimated by Scherrer equation.

° The BET method was used.

#### **Figure captions**

**Figure 1.** TEM and/or STEM/EDX images and Ru size distribution on the prepared catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/CeO<sub>2</sub>, (c) Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and (d) Ru/TiO<sub>2</sub>–CeO<sub>2</sub>.

**Figure 2.** H<sub>2</sub>-TPR profiles of the prepared catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/CeO<sub>2</sub>, (c) Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and (d) Ru/TiO<sub>2</sub>–CeO<sub>2</sub>.

**Figure 3.** CH<sub>4</sub> production of a three-run test over the catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/CeO<sub>2</sub>, (c) Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and (d) Ru/TiO<sub>2</sub>–CeO<sub>2</sub>. The reaction process for each run was carried out in a temperature range of 150–600 °C at a gas flow rate of 20 mL/min (5% CO<sub>2</sub>, 20% H<sub>2</sub>, and 75% Ar). The described process of each run was then sequentially repeated three times. For ease of recognition of the efficiency difference in catalysis, a small amount of catalyst (100 mg) was used for this experiment. When a larger amount of catalyst (1 g) was used, 100% conversion of CO<sub>2</sub> and 100% yield of CH<sub>4</sub> were easily achieved at 250 °C.

**Figure 4.** TEM images, HAADF-STEM images, and EDX mappings of Ce, Si, and Ru elements of the catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/CeO<sub>2</sub>, (c) Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and (d) Ru/TiO<sub>2</sub>–CeO<sub>2</sub> after the three-run test.

**Figure 5.** Ru particle size distributions in the as-prepared state and after the three-run test of the catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/SiO<sub>2</sub>–CeO<sub>2</sub>, and (c) Ru/TiO<sub>2</sub>–CeO<sub>2</sub>.

**Figure 6.** HAXPES Ce3d spectra of (a) commercial CeO<sub>2</sub>, (b) prepared CeO<sub>2</sub>, and (c) prepared TiO<sub>2</sub>–CeO<sub>2</sub>. The peak positions of Ce<sup>4+</sup> and Ce<sup>3+</sup> marked by yellow and green, respectively, were obtained from the literature [38,48].

**Figure 7.** CH<sub>4</sub> production of CO<sub>2</sub> methanation over (a) Ru/calcined CeO<sub>2</sub>, (b) Ru/calcined SiO<sub>2</sub>–CeO<sub>2</sub>, and (c) Ru/calcined TiO<sub>2</sub>–CeO<sub>2</sub>. The CO<sub>2</sub> methanation test was carried out in the temperature range of 150–600 °C at a gas flow rate of 20 mL/min (5% CO<sub>2</sub>, 20% H<sub>2</sub>, and 75% Ar). The reaction time for each temperature step was kept at 30 min.

**Figure 8.**  $CH_4$  yield of  $CO_2$  methanation using (a, b) Ru/CeO<sub>2</sub> and (c, d) Ru/TiO<sub>2</sub>–CeO<sub>2</sub> in the 10-cycle test at 50 °C and 300 °C (the graph represents only the results at 300 °C) and for 24 h at 400 °C, respectively. In each cycle of the 10-cycle test, the reaction time was 30 min at each reaction temperature of 50 °C and 300 °C. In the cases of (a) and (c), 100 mg of catalysts were used, while 25 mg of catalysts were used in the cases of (b) and (d) in expectation of earlier activity loss of the catalysts in the long-term stability tests.



Figure 1.







Figure 3.







Figure 5.



Figure 6.







Figure 8.