



Enhanced carbon resistance and regenerability in methane partial oxidation to syngas using oxygen vacancy-rich fibrous Pd, Ru and Rh/KCC-1 catalysts

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Received: 30 June 2020 / Accepted: 19 January 2021 / Published online: 9 February 2021

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Abstract

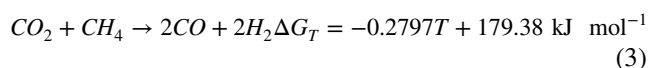
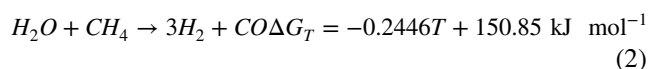
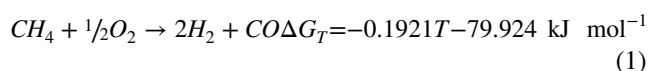
Rising concerns about petroleum depletion and energy demand are calling for alternative processes such as methane partial oxidation to produce syngas for downstream synthetic fuel production. However, industrial application is limited by catalyst deactivation caused by carbon deposition and reoxidation of active metals. Here we synthesized dendritic fibrous Pd, Ru and Rh/KAUST Catalysis Centre 1 (KCC-1) catalysts by microemulsion followed by wetness impregnation. Catalysts were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, electronic spin resonance, Fourier transform infrared spectroscopy and UV–Vis diffuse reflectance spectroscopy. We measured catalytic performance, stability and regenerability at 900 °C over 16 h-on-stream. Results reveal that oxygen vacancies into the KCC-1 framework enhance the interaction with noble metal particles, creating a strong metal–support interaction decreasing in the order Rh/KCC-1, Pd/KCC-1, Ru/KCC-1. Interestingly, CH₄ conversion followed the same order: 74–80% for Rh/KCC-1, 60–71% for Pd/KCC-1, 53–63% for Ru/KCC-1, without a significant carbon deposit. These findings mean that oxygen vacancies retained the metal in the active metallic phase and prevented carbon deposits. Overall, metal/KCC-1 is as bifunctional catalyst whereby oxygen vacancies generate labile electrons contributing to electrostatic metal–support interactions, stabilization of metal phases and providing labile oxygen ions for carbon gasification.

Keywords Oxy-reforming of methane · Noble metal · Fibrous silica · Synthetic gas · Oxygen vacancy · KCC-1-supported catalyst

Introduction

Environmental concerns and intensive rise of global energy demand have driven researchers to explore alternative energy source for replacing current fossil fuel-based energy system (Abdulrasheed et al. 2019; Minh et al. 2018; Pham et al. 2020; Osman et al. 2020). Syngas appears as the prospective alternative since it provides versatile building blocks

for yielding high value-added products such as long-chained hydrocarbon, petrochemical and oxygenated compounds (Minh et al. 2018; Herminio et al. 2020). Among the technologies, methane partial oxidation (Eq. 1) offers promising advantages, including provides (i) an effectual and fast CH₄ conversion due to the short contact time, (ii) mildly exothermicity for excellent energy efficiency, (iii) an ideal ratio of H₂ to CO around 2 for downstream Fischer–Tropsch synthesis without necessity of auxiliary separation processes (Bashan and Ust 2019; Elbadawi et al. 2020).

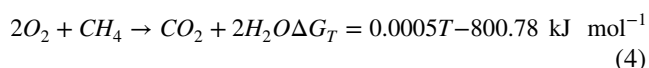


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Depending on the reaction conditions, transition metal-catalyzed methane partial oxidation reportedly proceeds through total oxidation of CH_4 (Eq. 4), followed by CH_4 reforming processes involving methane steam reforming (Eq. 2) and methane dry reforming (Eq. 3), known as indirect combustion-reforming route (Liu et al. 2007; Enger et al. 2008). The noble metal catalysts are attractive candidates to catalyze methane partial oxidation, accredited to their remarkable ability of C–H bonds cleavage for CH_4 molecule (Zhu et al. 2013; Dou et al. 2018). Fundamentally, high reaction temperature and intensive gaseous environment are the prerequisites for achieving high CH_4 conversion and high purity of syngas. However, the alteration of both local structure and oxidation state for noble metal catalysts at harsh reaction conditions is the great challenges toward the catalyst stability (Enger et al. 2008). Additionally, high reaction temperature thermodynamically favors the formation of carbon deposits via CH_4 decomposition, posing the occurrence of catalyst deactivation (Argyle et al. 2015; Qin et al. 2020).

From the above reasons, the ideal catalysts for methane partial oxidation are perceived to possess great metal–support interaction and high surface oxygen mobility against carbon deposition and metal sintering. Micro- or mesoporous siliceous materials are extensively employed as the support owing to their confinement effect of ordered mesoporous structures anchoring the metal particles inside the channels (Fajardo et al. 2010; Li et al. 2018; Singh et al. 2018). However, these complex mesopore networks engender diffusion resistance of intraparticle which adversely affects the accessibility of reactants to active sites. In addition, these materials tend to encounter mesopore channels blockage due to metal agglomeration inducing the loss of catalyst activity under long-term reaction run (Siang et al. 2019; Li et al. 2018). Thus, enormous efforts have been dedicated in the development of advanced modification for these siliceous materials to address the aforementioned problems.

Silica-based dendritic fibrous KAUST Catalysis Centre 1 (KCC-1) material with hierarchical pores and three-dimensional center-radial channels has recently appeared as a rising star for catalytic heterogeneous system owing to its unique fibrous morphology providing large surface area, open pore nanochannels, highly accessible internal spaces and active sites resulting in excellent activity in catalysis (Wang et al. 2019). In our earlier work (Siang et al. 2020a), we have studied the important role of oxygen vacancies in KCC-1 on the noble metal-catalyzed methane partial oxidation performance. Herein, we report the catalytic behavior of dendritic fibrous M (M = Pd, Rh or Ru)/KCC-1 catalysts for methane partial oxidation stability test

with reducing–oxidizing cycle. Particularly, the main objective of the current research was to inspect the role of oxygen vacancies in M/KCC-1 catalysts with respect to their physicochemical properties and catalytic performances for the methane partial oxidation at long-term integrated operating conditions.

Experimental

Catalyst preparation

Microwave-supported microemulsion technique was applied for preparing dendritic fibrous silica-based support (named KCC-1). The solution consisted of distilled water (737.7 mL), urea (14.9 g) and hexadecyltrimethylammonium bromide (CTAB, 23.8 g) was thoroughly mixed for 0.5 h at room temperature. In addition, another solution contained toluene (731.8 mL), 1-butanol (31.2 mL) and tetraethyl orthosilicate (63.4 g) was prepared and subsequently mixed with the former solution at 25 °C for 0.5 h. The subsequent milky mixture was subjected into oven for exposure to discontinuous microwave radiation (400 W) for 4 h at 120 °C and then cooled down to 25 °C. The mixture was air-dried at 110 °C for 24 h inside an oven and was calcined inside a furnace for 6 h at 900 °C to produce the dendritic fibrous KCC-1 support.

The 0.5 wt% M (M = Ru, Pd, Rh)-loaded KCC-1 catalysts were synthesized by a common wetness impregnation approach. The dendritic fibrous KCC-1 support (2.985 g) and accurately calculated precursors of noble metal oxide (0.025 g of PdCl_2 ; 0.031 g of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$; 0.031 g of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$) were dispersed in distilled water (30 mL). The mixtures were well-stirred for 2 h at 60 °C before air-dried overnight at 110 °C. The resultant solid powders were air-calcined for 6 h at 900 °C to yield the M/KCC-1 catalysts.

Characterization methods

Surface morphology of specimen was assessed through transmission electron microscopy (TEM) measurements and field emission scanning electron microscopy (FESEM) by JEOL JEM-2100F and Zeiss Supra VP35 system, respectively. X-ray diffraction (XRD) measurement was taken by D8 Advance Bruker diffractometer at 45 kV and 40 mA with 1.544 Å of Cu K α radiation to identify the crystallinities of specimens before and after reaction. The scanning range of 2θ from 2 to 80° (scanning rate = 0.1°, step size = 0.05°) was selected for collection. Electronic spin resonance (ESR) measurement was taken by employing JEOL JES-FA100 ESR spectrometer to ascertain the oxygen vacancies and surface defects of specimen. An Agilent Cary 640 spectrometer was employed to collect the Fourier transform infrared (FTIR) spectrum of specimen

by using potassium bromide (KBr) method at room temperature in a range of 400–4000 cm^{-1} with resolution of 5 cm^{-1} . The UV–Vis diffuse reflectance spectroscopic (UV–Vis DRS) measurement was taken by Agilent Cary 60 UV–Vis DRS spectrophotometer to record the spectrum of sample in a range of 200 to 800 nm at 25 °C. The nature of carbon deposit on spent catalysts was assessed by a Raman spectrometer (Renishaw InVia) armed with a laser beam (633 nm). A range from 100 to 3000 cm^{-1} was selected to record the Raman spectra of specimen.

Catalytic evaluation of methane partial oxidation

The time-on-stream stability tests were inspected at 900 °C with CH_4/O_2 molar ratio of 2:1 under 1 atm over a duration of 8 h, followed by in situ oxidation in 50% O_2/N_2 flow for 3 h before swapping back to reaction gas for another 5 h of reaction. Pelletized catalysts (0.2 g) with average catalyst particle size of 150 μm were in situ reduced for 2 h in H_2 flow (20 mL min^{-1}) at 900 °C, followed by N_2 gas stream (60 mL min^{-1}) for 0.5 h. A 30,000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ of gas hourly space velocity (GHSV) was deployed for each run. The effluent gases at the reactor outlet were analyzed by on-line GC system (Agilent 7820 N) equipping Carboxen 1010 column and thermal conductivity detector (TCD).

The catalytic performances of M/KCC-1 catalysts were evaluated in respect of CH_4 conversion (X_{CH_4}), CO_2/CO ratio, H_2/CO ratio, carbon deposition rate and carbon balance as provided in following Eqs. (5) to (9).

$$X_{\text{CH}_4}(\%) = \frac{F_{\text{CH}_4}^{\text{In}} - F_{\text{CH}_4}^{\text{Out}}}{F_{\text{CH}_4}^{\text{In}}} \times 100\% \quad (5)$$

$$\text{H}_2/\text{CO} = \frac{F_{\text{H}_2}^{\text{Out}}}{F_{\text{CO}}^{\text{Out}}} \quad (6)$$

$$\text{CO}_2/\text{CO} = \frac{F_{\text{CO}_2}^{\text{Out}}}{F_{\text{CO}}^{\text{Out}}} \quad (7)$$

$$\text{Carbon balance}(\%) = \frac{F_{\text{CH}_4}^{\text{Out}} + F_{\text{CO}}^{\text{Out}} + F_{\text{CO}_2}^{\text{Out}}}{F_{\text{CH}_4}^{\text{In}}} \times 100\% \quad (8)$$

$$\begin{aligned} &\text{Rate of carbon deposition} (\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}) \\ &= \left(1 - \frac{F_{\text{CH}_4}^{\text{Out}} + F_{\text{CO}}^{\text{Out}} + F_{\text{CO}_2}^{\text{Out}}}{F_{\text{CH}_4}^{\text{In}}} \right) \times \frac{F_{\text{CH}_4}^{\text{In}}}{W_{\text{Cat}}} \end{aligned} \quad (9)$$

where W_{cat} is the catalyst weight (g), while F^{Out} and F^{In} represent the outlet and inlet molar flow rates (mol s^{-1}), respectively.

Results and discussion

Catalyst characterization

Surface morphology and crystallinity studies

Figure 1a displays the X-ray diffractograms of specimens within a range from 20 to 80°. A wide and intensive diffraction band at 2 θ of 20–30° assigned to the amorphous silica framework (JCPDS card No. 29-0085) was detected for all specimens, demonstrating the overall structural integrity of fibrous KCC-1 framework after addition of noble metal particles. However, the insignificant reduction observed in the peak intensity of silica for all three catalysts indicated a slight distortion of fibrous KCC-1 framework with the metal embedment. For the XRD pattern of Ru/KCC-1 catalyst, three peaks found at 2 θ of 28.4°, 34.9° and 54.4° were corresponding to (1 1 0), (1 0 1) and (2 1 1) planes of RuO_2 (JCPDS card No. 46-1215) (Muñoz-Murillo et al. 2018). The discerned small peak for Pd/KCC-1 catalyst at 2 θ of 34.1° was attributed to the (1 0 1) PdO plane (JCPDS card No. 41-1107) (Yang et al. 2017). The absence of typical peaks for Rh_2O_3 in the XRD pattern of Rh/KCC-1 catalyst indicated the well dispersion of Rh_2O_3 particles resulting in small crystalline size that is beyond XRD detection limit.

The surface morphology of fibrous KCC-1 support was assessed by FESEM and TEM measurement as displayed in Fig. 1B–1E. KCC-1 support presented spherical well-ordered microspheres with dendrimeric morphology (Fig. 1b), while the average particle size distribution was calculated to be 575.8 nm (Fig. 1b) optimal for the application of heterogeneous catalytic systems (Bayal et al. 2016; Maity et al. 2019). The illustration of the TEM (Fig. 1d) indicated that the fibrous spherical KCC-1 originated from the micro-spheric centers and formed uniformly in every axial direction. In addition, a close inspection of TEM image (Fig. 1e) confirmed the successful development of dendrimeric silica fibers at KCC-1 outer surface which improves the approachability of reactants to the inner surface.

As seen in the TEM images (Figs. 1f–h), the incorporation of noble metal oxides retained the structural morphology of fibrous KCC-1 support. The particle size for Pd/KCC-1, Ru/KCC-1 and Rh/KCC-1 was determined as 9.68 nm, 10.14 nm and 6.26 nm, respectively. Figure 1f displays the crystalline lattice of RuO_2 phase with d-spacings of 0.251 nm and 0.315 nm corresponding to the (1 0 1)

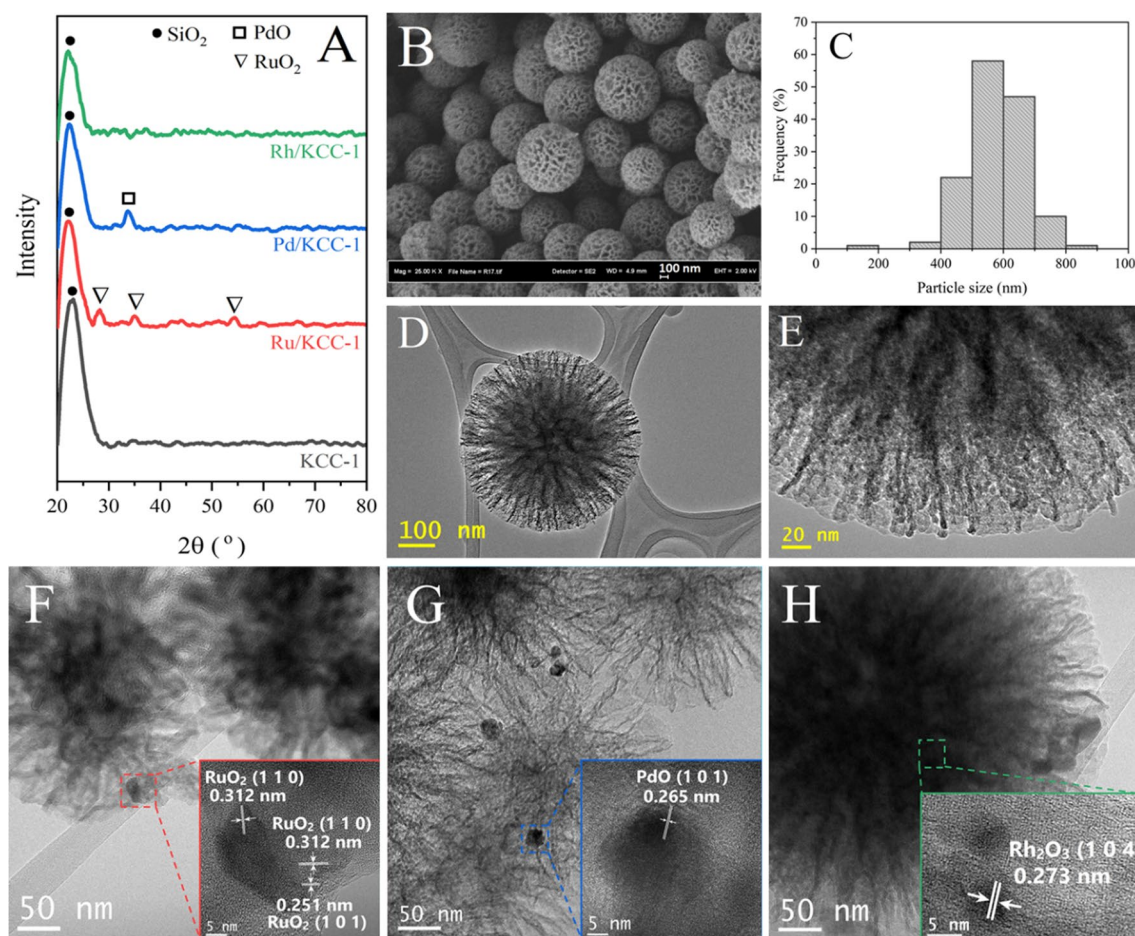


Fig. 1 **a** X-ray diffractograms of bare KAUST Catalysis Centre 1 (KCC-1) support and M/KCC-1 (M=Ru, Pd, Rh) catalysts. **b** Field emission scanning electron microscopy image and **c** particle size distribution of fibrous KAUST Catalysis Centre 1 (KCC-1) support. Transmission electron microscopy images of **d** fibrous KAUST Catalysis Centre 1 (KCC-1) microsphere, **e** dendrimeric silica fibers of KAUST Catalysis Centre 1 (KCC-1), **f** Ru/KAUST Catalysis Centre 1

(Ru/KCC-1), **g** Pd/KAUST Catalysis Centre 1 (Pd/KCC-1) and **h** Rh/KAUST Catalysis Centre 1 (Rh/KCC-1) catalysts. Note the dendrimeric silica fibers are successfully formed by using microwave-assisted microemulsion technique and the structural integrity of KAUST Catalysis Centre 1 (KCC-1) is affirmed after noble metal addition. The lattice fringes of noble metal oxides are determined which is in accordance with the corresponding X-ray diffraction crystalline planes

and (1 1 0) crystal planes (Zhang et al. 2019). The lattice fringe of 0.265 nm ascribed to the (1 0 1) crystal facet of PdO phase (Lee et al. 2020) is found in Fig. 1g, while Fig. 1h shows the lattice fringe of 0.273 nm belonging to the (1 0 4) Rh₂O₃ plane (Staerz et al. 2017). These observations were in line with the XRD results. In addition, the HRTEM mappings (Fig. S1) for all M/KCC-1 catalysts corroborated the well dispersion of the noble metals including RuO₂, PdO and Rh₂O₃ on the surface of KCC-1.

Surface defect studies

As displayed in Fig. 2a, the appearance of three ESR signals at $g = 1.91$, 1.95 and 1.99 corroborated the presence of oxygen vacancies in all specimens. In particular, the observed

prominent axial ESR signals at $g = 1.91$ and 1.99 were correspondingly attributed to the paramagnetic oxygen vacancies and localized unpaired electron-defective metal cations (Hamid et al. 2018; Teh et al. 2016).

In fact, the detected g -values in a range of 1.99–1.91 could be ascribed to the vibrational mode of non-bridging oxygen hole centers (NBOHCs) in KCC-1 material. These holes offer a platform for transformation of bulk SiO₂ to SiO_x (where x is lesser than 2) leading to the growth of NBOHCs ($\equiv\text{Si}-\text{O}^*$) with unpaired electrons or hanging bonds, also known as E' centers ($\equiv\text{Si}^*$) (Jafarzadeh et al. 2012; Hamid et al. 2017). These radical sites of silica are believed to serve as active site for effectively adsorbing oxidants (viz., CO₂, O₂ and H₂O) on catalyst surface, which eventually enhances the surface reaction with adsorbed

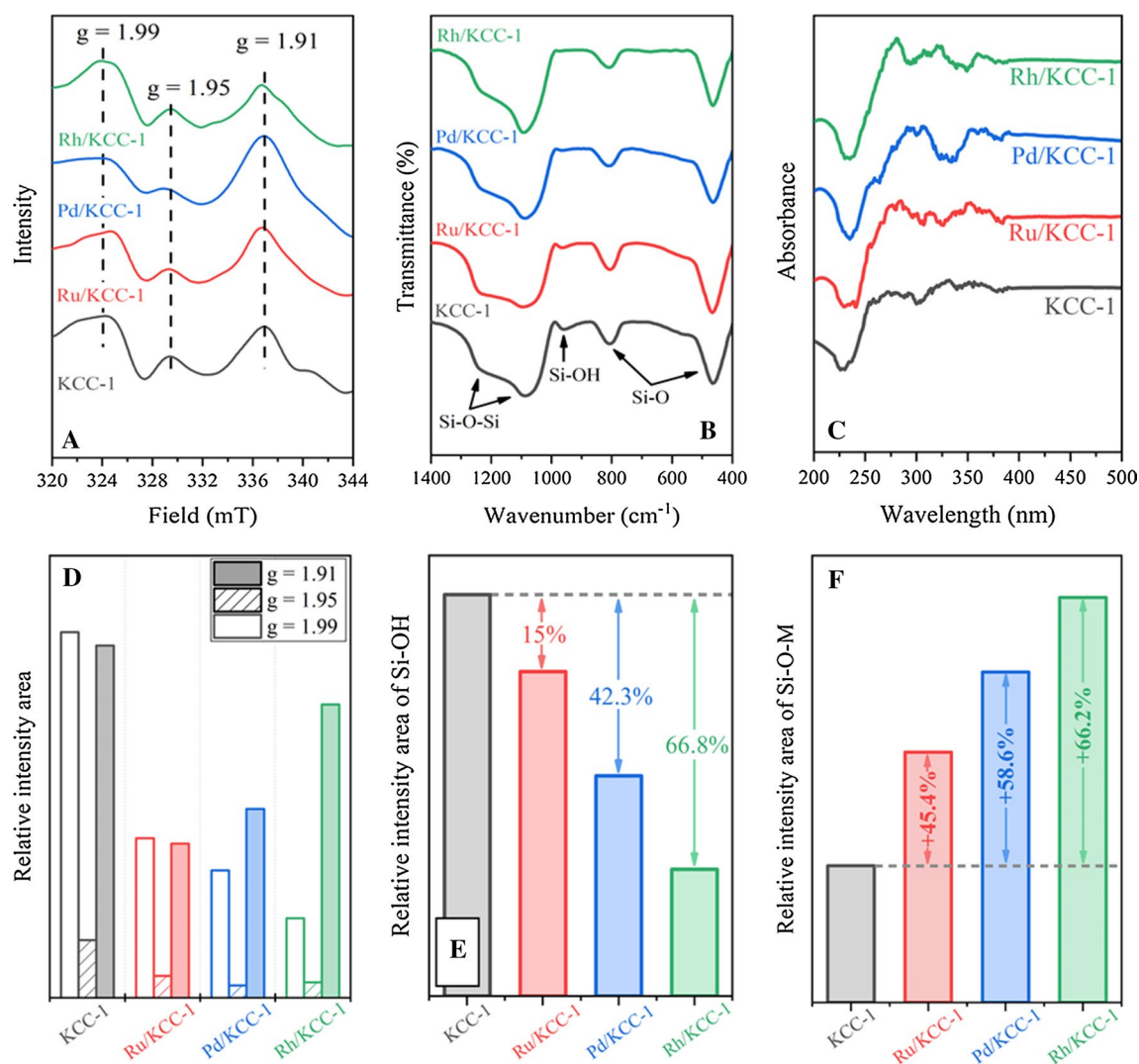


Fig. 2 **a** Electronic spin resonance spectra, **b** Fourier transform infrared spectroscopy spectra and **c** ultraviolet–visible diffuse reflectance spectroscopy spectra of KAUST Catalysis Centre 1 (KCC-1) support, Ru/KAUST Catalysis Centre 1 (Ru/KCC-1), Pd/KAUST Catalysis Centre 1 (Pd/KCC-1) and Rh/KAUST Catalysis Centre 1 (Rh/KCC-1) catalysts. Relative intensity area of **d** electronic spin resonance spectra, **e** Fourier transform infrared spectroscopy spectra and **f** ultraviolet–visible diffuse reflectance spectroscopy spectra for catalysts at specific location. Note that the metal–support interaction strength dropped in the order of Rh/KCC-1 > Pd/KCC-1 > Ru/KCC-1 based on the difference in their intensity areas of electronic spin resonance, Fourier transform infrared spectroscopy and ultraviolet–visible diffuse reflectance spectroscopy signals

CH_x (where $0 < x \leq 3$) from CH_4 molecules on metal particles and, thus, promotion of syngas yield via methane dry reforming and methane steam reforming (Mihai et al. 2012; Cheng et al. 2016). Moreover, the role of oxygen vacancies is reportedly essential to basicity strength. The formation of oxygen vacancies produces two unpaired electrons, creating a strong Lewis basicity of surface, and subsequently contributes to an improvement in CO_2 adsorption and dissociation (Teh et al. 2016).

Based on the literature (Morazzoni et al. 1990), a paramagnetic oxygen vacancy (V_{O}^+ , at $g = 1.91$) and an electron can be readily formed through ionization of a neutral oxygen

vacancy site. The subsequent labile electrons mobilize to the adjacent unpaired electron-deficient metal cations (at $g = 1.99$), hence creating the electrostatic interactions. By using this characteristic, the metal–support interaction strength between the oxygen vacancies and noble metal particles can be deduced through the difference in relative intensity areas of the ESR signals. As seen in Fig. 2d, noble metal addition on KCC-1 surface inevitably resulted in a decline in all ESR signals characteristic for oxygen vacancies of KCC-1. Among the catalysts, the interaction strength between KCC-1 and noble metals is predictably declined by following the order of Rh/KCC-1 > Pd/KCC-1 > Ru/KCC-1.

To further verify the above speculation, KBr-FTIR analyses were performed as shown in Fig. 2b. Regardless of noble metal addition, the FTIR spectra of all specimens exhibited a broad and intensive band in a range of 1400 cm^{-1} to 1000 cm^{-1} with a substantial shoulder at 1240 cm^{-1} , which was attributed to the asymmetric Si–O–Si stretching vibrations (Siang et al. 2019; Bukhari et al. 2019). The detected peaks at 806 cm^{-1} and 462 cm^{-1} could be assigned to asymmetric and symmetric Si–O stretching vibrations, while the transmittance band of Si–OH vibrations was discerned at 968 cm^{-1} (Siang et al. 2019; Abdulrasheed et al. 2019). Based on the literature (Hamid et al. 2018; Bukhari et al. 2019), the extent of the interaction between metal ions and siliceous material support (i.e., Si–O–M) can be estimated by the intensity area of Si–OH bond at 968 cm^{-1} . The peak intensities of Si–OH bond for M/KCC-1 catalysts were noticeably reduced compared to the bare KCC-1, indicating Si–O–M formation via desilication, in which the O–Si and O–H in KCC-1 structure was replaced by metallic ions (i.e., Ru, Pd or Rh). From the decrease in Si–OH intensity (Fig. 2e), the order of metal–support interaction strength for the catalysts was similar to the postulation obtained from ESR results.

Such deduction was also supplemented by the results of UV–Vis DRS measurement for M/KCC-1 catalysts (Fig. 2c). The band at 200–240 nm was ascribed to the neutral oxygen associated with oxygen vacancy ($\equiv\text{Si}-\text{Si}\equiv$) and twofold-coordinated silicon ($-\text{O}-\text{Si}-\text{O}-$), whereas the observed band across 300–400 nm suggested the existing light-emitting non-bridging oxygen hole center (Jafarzadeh et al. 2012). These observations further verified the presence of oxygen vacancies in KCC-1 for all catalysts, which was consistent with ESR results. In fact, the appearance of band at 200–240 nm was possibly indicative of the chemical bonds between O atom in KCC-1 framework and noble metal particles for M/KCC-1 catalysts (Bukhari et al. 2019). Thus, the change in the intensity area of band at 200–240 nm could reveal the degree of Si–O–M formation of M/KCC-1 catalysts. As shown in Fig. 2f, the Rh/KCC-1 possessed the highest degree of Si–O–M formation compared to Ru/KCC-1 and Pd/KCC-1, indicating the better metal dispersity (Fig. S1) and relatively higher metal–support interaction. By considering the results from ESR, KBr-FTIR and UV–Vis DRS, the order of metal–support interaction strength of catalysts was affirmed as Rh/KCC-1 > Pd/KCC-1 > Ru/KCC-1. A greater metal–support interaction reportedly induces spillover effect due to lowered activation energy barrier of reactants' dissociation and, thus, improvement of product formation rate (Pan et al. 2017). Therefore, the Rh/KCC-1 is estimated to be the optimum catalyst, exhibiting the highest catalytic performance among the KCC-1-supported catalysts.

Evaluation of time-on-stream reaction performance and stability

Figure 3 depicts the time-on-stream stability profile of M/KCC-1 catalysts over 8-h reaction run in terms of CH_4 conversion, H_2/CO and CO_2/CO ratios. All three catalysts showed good robustness and performance in the above-mentioned reaction parameters. Although all three catalysts exhibited a similar catalytic behavior in time-on-stream stability test, there are substantial disparities. In particular, the CH_4 conversion was stable over 8 h at ~ 53 –63% for Ru/KCC-1 (Fig. 3a), ~ 60 –71% for Pd/KCC-1 (Fig. 3b) and ~ 74 –80% for Rh/KCC-1 (Fig. 3c). The difference in CH_4 conversion obtained over M/KCC-1 catalyst is closely related to their M–O bond strength depending on the different degree of the formation energy (Zhu et al. 2013). According to the literature (Zhu et al. 2013; Siang et al. 2020b; Liu et al. 2008), Rh–O bonds possess the highest formation energy, followed by Pd–O and Ru–O bonds, respectively, suggesting that Rh/KCC-1 catalyst has the lowest propensity toward oxidation among the catalysts. The preservation of metallic Rh^0 form effectually reduced the activation energy of C–H dissociation for CH_4 molecules, thus resulting in the highest CH_4 conversion over 8 h-on-stream reaction run (Fig. 3a). Notably, noble metal particles in M/KCC-1 catalysts mostly presented as active metallic noble metal phase under the greatly reducing surrounding (i.e., H_2 and CO) of methane steam reforming and methane dry reforming.

To scrutinize the probable impacts of the oxidation states of noble metal particles on reaction performance and the necessity of H_2 reduction pretreatment for M/KCC-1 catalysts before reaction, consecutive experiments of in situ oxidation (50% O_2/N_2 flow at 900°C for 3 h) were promptly performed over the spent M/KCC-1 catalysts followed by changing back to reaction gas. As shown in Fig. 3a–c, all three catalysts exhibited complete restoration of their catalytic performances in a short time as compared to their stable behavior (at 4–8 h) before the in situ oxidation process. This revealed that M/KCC-1 catalysts preserved their stability after subjected to oxidative environment at high temperature and, most importantly, much of the active sites, presumably metallic noble metal forms (i.e., Ru^0 , Pd^0 and Rh^0) on KCC-1 support were facilely regenerated after exposure to reaction gas, as supplemented by the post-reaction XRD measurement in the following section. The unnecessary of H_2 reduction pretreatment and the excellent stability for the reducing–oxidizing cycles are of significance to the employment of KCC-1-supported noble metal catalysts for methane partial oxidation application.

In addition, Fig. 3 displays the CO_2/CO and H_2/CO ratios over M/KCC-1 specimens as a function of 16 h-on-stream.

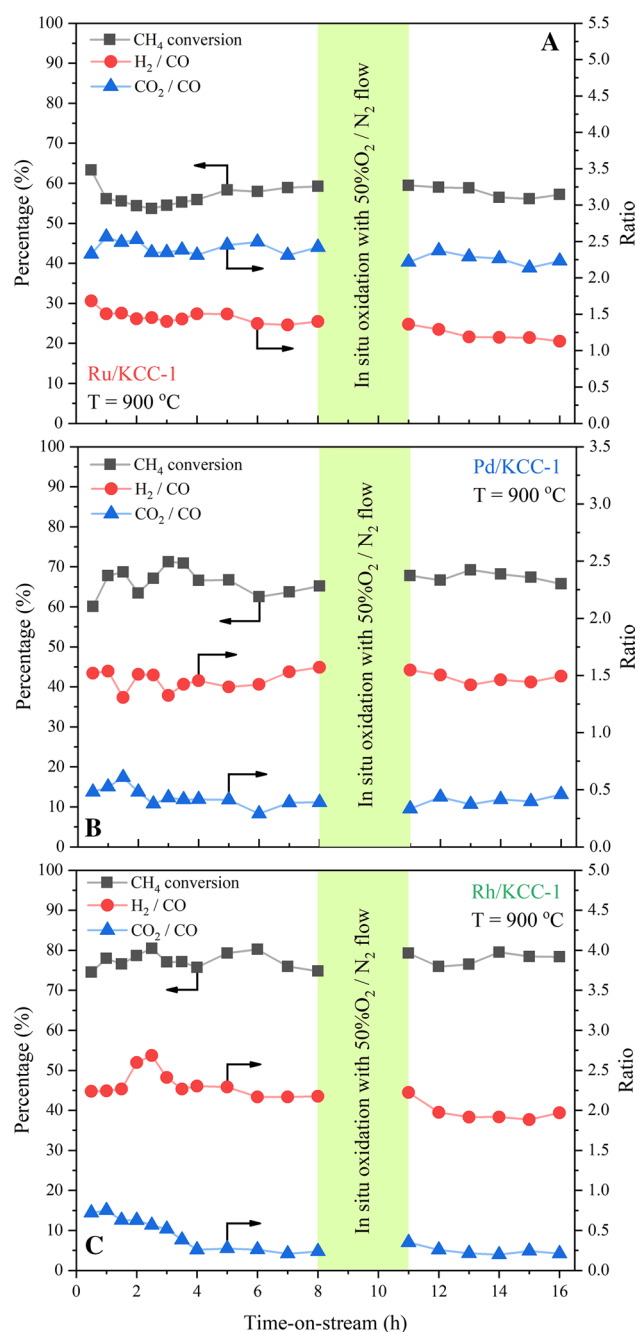


Fig. 3 H_4 conversion, H_2/CO ratio and CO_2/CO ratio for **a** Ru/KAUST Catalysis Centre 1 (Ru/KCC-1), **b** Pd/KAUST Catalysis Centre 1 (Pd/KCC-1) and **c** Rh/KAUST Catalysis Centre 1 (Rh/KCC-1) catalysts as a function of time-on-stream at 900 °C with CH_4/O_2 molar ratio of 2 under atmospheric pressure. The complete restoration of reaction activity following a 3-h in situ oxidation with 50% O_2/N_2 flow (100 mL min^{-1}) at 900 °C. Note the all three catalysts exhibit complete restoration of their catalytic performances in a short duration, suggesting the excellent regenerability of metallic noble metal forms (i.e., Ru^0 , Pd^0 and Rh^0) on KAUST Catalysis Centre 1 (KCC-1) support after exposure to reaction gas

Notably, for the cases of Pd/KCC-1 (Fig. 3b) and Rh/KCC-1 (Fig. 3c), the H_2/CO ratios were always greater than the CO_2/CO ratio, implying the enhancement of CO_2 and H_2O uses in the syngas production and suppression on carbon formation. Nevertheless, the Ru/KCC-1 showed an opposite trend, in which the CO_2/CO ratio was higher than H_2/CO ratio throughout the time-on-stream stability test, as a result of the deposition of amorphous carbon. This reflected that the concentration level of oxygen vacancies could vary the order of the H_2/CO and CO_2/CO ratios. The growth in the H_2/CO ratio from low to higher concentration of oxygen vacancies in M/KCC-1 ($\text{Ru/KCC-1} < \text{Pd/KCC-1} < \text{Rh/KCC-1}$) with a concomitant decrease in the ratio of CO_2 to CO , further corroborates that KCC-1 support-induced modifications of the noble metal surface chemistries are the main contributory factors responsible for this observation. Remarkably, the practical ratio of H_2 to CO around 2 can be achieved over the Rh/KCC-1 catalyst, which is of importance to the downstream industrial synfuel production without the necessity of separation and purification processes.

Nature and quantity of carbon deposit after reaction

Post-reaction X-ray diffractograms and Raman spectroscopy measurements were conducted to distinguish the nature of coke deposit on surface of spent M/KCC-1 catalysts, and the relevant results are shown in Fig. 4. As displayed in Fig. 4a, an analogous broad curve of amorphous SiO_2 in a range of $15\text{--}30^\circ$ was observed for three spent catalysts, suggesting the preservation of siliceous framework of KCC-1 support after high-temperature reaction. Notably, the absence of characteristic peak attributed to graphitic carbon at 2θ of 26.6° (JCPDS card No. 75-1621) suggested that dendritic fibrous M/KCC-1 catalysts were utterly free from graphite (Siang et al. 2020a). This could be a result of high concentration of oxygen vacancies continuously provided labile oxygen ions from lattice O^{2-} species to facilitate the carbon gasification process, hence inhibiting the graphitization on catalyst surface under oxidative environment (Siang et al. 2020a).

In addition, for spent Ru/KCC-1, the diffraction peaks located at 2θ around 28.4° and 54.4° were assigned to (1 1 0) and (2 1 1) crystal planes of RuO_2 (JCPDS card No. 46-1215), whereas the 2θ of 38.5° , 43.9° , 58.5° and 63.4° was corresponded to (1 0 0), (1 0 1), (1 0 2) and (1 1 0) metallic Ru^0 crystal planes (JCPDS card No. 01-1253) (Li et al. 2010). For spent Pd/KCC-1, the distinctive peaks at $2\theta = 33.6^\circ$ and 54.9° represented the presence of (0 0 2) and (1 1 2) PdO crystal planes (JCPDS card No. 41-1107), while the peaks at 2θ of 39.8° and 63.6° were attributed to the (1 1 1) and (2 2 0) crystal planes of metallic Pd^0 , correspondingly (Lin et al. 2014). For spent Rh/KCC-1, the characteristic

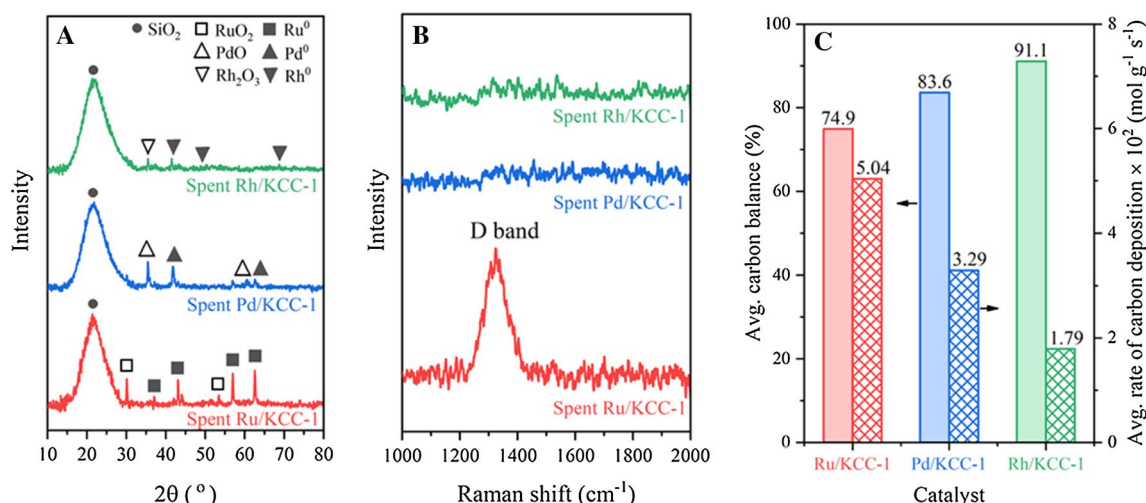


Fig. 4 **a** X-ray diffractograms and **b** Raman spectra of spent Ru/KAUST Catalysis Centre 1 (Ru/KCC-1), Pd/KAUST Catalysis Centre 1 (Pd/KCC-1) and Rh/KAUST Catalysis Centre 1 (Rh/KCC-1) catalysts after stability test at 900 °C and with CH₄/O₂ molar ratio of 2 under atmospheric pressure. **c** Correlation between average rate

peak corresponded to (1 0 4) crystal plane of Rh₂O₃ was discerned at 2θ about 32.8°, while the peaks positioned at 2θ of 41.1°, 47.8° and 69.8° were correspondingly ascribed to several planes of metallic Rh⁰, namely (1 1 1), (2 0 0) and (2 2 0) (Zou et al. 2015). The co-existence of metal oxides (i.e., RuO₂, PdO and Rh₂O₃) and their corresponding metallic form (viz., Ru⁰, Pd⁰ and Rh⁰) in the X-ray diffractograms of spent M/KCC-1 catalysts revealed that most of active metallic noble metal form were largely preserved possibly due to the existence of reducing gases (i.e., H₂ and CO) even at oxidative surrounding.

As seen in Fig. 4b, Raman spectrum of spent Ru/KCC-1, the only major absorption peak detected at band of 1325 cm⁻¹ (D band) implied the existence of heterogeneity of carbon deposit on catalyst surface. Specifically, the appearance of D band was triggered by amorphous carbon or carbon nanofilament (CNF) comprising of deficient sp³-bonded carbon atoms (Siang et al. 2018). Notably, the Raman spectra of both spent Rh/KCC-1 and Pd/KCC-1 showed that they were free from carbon deposition since no characteristic peaks corresponded to the vibration modes of carbonaceous species were observed. To justify the correlation between the concentration of oxygen vacancies in M/KCC-1 catalysts and their catalytic stability performance associated with carbon deposition, the comparison between average carbon deposition rate and average carbon balance for all three catalysts is summarized in Fig. 4c. Although the post-reaction XRD and Raman results revealed that all catalysts were apparently free from graphitic carbon, there is significant difference. It is noting that the average carbon balance increased in the order Ru/KCC-1 (74.9%) < Pd/KCC-1

of carbon deposition and average carbon balance. Note that all three spent catalysts are free from the graphitic carbon owing to the high concentration of oxygen vacancies, which is the key factor for achieving the excellent stability and regenerability

(83.6%) < Rh/KCC-1 (91.1%). This suggested that the rising discrepancy between concentration of oxygen vacancies and average rate of carbon deposition could result in the opposite order to the average carbon balance. Thus, the high density of oxygen vacancies in catalyst has the lowest tendency to accumulate carbon deposit, as evident by calculated average carbon deposition rate in Fig. 4c. Such behavior indicated that the oxygen vacancies in KCC-1-supported catalysts not only strengthened the metal–support interaction to enormously activate the dissociation of reactants for surface reaction but also provided labile oxygen ions from lattice O²⁻ species to greatly hinder the carbon deposition under oxidative surrounding, leading to a bifunctional reaction mechanism.

Conclusion

The dendritic fibrous M/KCC-1 (M = Pd, Ru, Rh) catalysts were synthesized by using microwave-supported microemulsion followed by conventional wetness impregnation methods and were tested for time-on-stream stability. FESEM and TEM images affirmed the successful formation of fibrous morphology with dendrimeric silica fibers at KCC-1 external surface. ESR spectroscopy analyses revealed that the concentration of oxygen vacancies in KCC-1 has substantial impact on the metal–support interaction regarding the catalytic performances of M/KCC-1 catalysts, by coupling with the FTIR and UV–Vis DRS results. The optimal catalyst was Rh/KCC-1 with respect to the CH₄ conversion and H₂/CO ratio in the time-on-stream stability test. The difference in

catalytic activity among M/KCC-1 catalysts was attributed to their M–O bond strength associated with the different degree of the formation energy. The reducing–oxidizing cycle in stability test corroborated that most of the metallic noble metal forms (i.e., Ru⁰, Pd⁰ and Rh⁰) on KCC-1 support were readily regenerated after exposure to reaction gas. The practical ratio of H₂/CO about 2 was achieved by the Rh/KCC-1 catalyst apposite for the downstream industrial synfuel production. No graphitic carbon was identified over the three spent catalysts, suggesting the high concentration of oxygen vacancies enormously suppressed carbon deposition via carbon gasification process by continuously providing labile oxygen ions from lattice O^{2−} species. The oxygen vacancies of M/KCC-1 catalysts evidently not only improved the metal–support interaction for activating and preserving the active metallic noble metal species but also generated labile oxygen ions to greatly suppress the carbon deposition under oxidative surrounding, leading to a bifunctional reaction mechanism.

Supplementary Information The online version contains supplementary material available at (<https://doi.org/10.1007/s10311-021-01192-0>).

Acknowledgements The financial aids from Universiti Teknologi Malaysia through Transdisciplinary Research Grant (No. 06G52 and 06G53) and the Universiti Teknologi Malaysia Zamalah Scholarship (Tan Ji Siang) for conducting this work are gratefully acknowledged.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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