Spectroscopic Characterization and Catalytic Activity of Rh Supported on CeO₂-Modified Al₂O₃ for Low-Temperature Steam Reforming of Propane

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Abstract

The present work aims at clarifying the effects of CeO₂ addition to Al₂O₃ support on the surface chemical characteristics and catalytic activity of supported Rh catalysts for low-temperature steam reforming of propane. Steam reforming of propane was carried out at 500 °C over Rh catalysts supported on alumina modified with different CeO₂ loading (0, 5, 10, 20, 50, 75, and 100 wt%). The Rh catalyst supported on 20 wt% CeO₂-modified alumina (2Rh/20CeAl) showed the highest propane and steam conversions, followed in decreasing order by those with 10, 5, 50, 75, 0, and 100 wt% CeO₂. TPR results show that the interaction between ceria and rhodium improves the reducibility of both rhodium oxide and ceria. XPS analysis indicates strong ceria-alumina interaction and strong Rh-support interaction for Rh catalysts with CeO₂ loading less than 20 wt%. Field-Emission SEM and AES results revealed that at 20 wt% CeO₂ loading, ceria was dispersed as separate nano-particles with sizes of 100 - 200 nm on the alumina surface. At high CeO₂ loading (≥ 50 wt%) ceria particles

formed conglomerates covering alumina surface. The 2Rh/20CeAl catalyst showed the highest activity for propane steam reforming possibly because the high CeO₂ dispersion created a large area of ceria-alumina interface which helped increase Rh dispersion, and the strong interaction between Rh and support helped enhance the reducibility of ceria and rhodium oxide. Rh loaded onto the interfacial region of ceria and alumina is considered to be most active for the 2Rh/20CeAl catalyst.

Keywords: Catalyst; Rh; Alumina; Ceria loading; Steam reforming; Propane

1. Introduction

Due to the high intrinsic efficiency of fuel cells for auxiliary power supply [1-3], steam reforming of hydrocarbon fuels plays a key role in on-site and on-board hydrogen production and in fuel cells for developing clean energy technologies and protecting the environment. Steam reforming of liquid hydrocarbon fuels such as jet fuels and diesel fuels is an effective way for hydrogen production due to their high energy densities and existing infrastructure. However, thermal decomposition of heavy hydrocarbons to form carbonaceous deposits is a main issue under conventional reforming conditions [2]. In order to improve the energy efficiency and reduce the thermal decomposition in steam reforming process, low-temperature reforming (400 - 650 °C), or pre-reforming, has been suggested as an additional process step by which fuel saving could be increased by 9% relative to the process without the pre-reformer [4-6]. The major role of the pre-reformer is to convert heavier hydrocarbons to methane and synthesis gas and prevent coking. After pre-reforming, methane steam reforming may be applied at high temperature (750 - 800°C) either for producing

hydrogen or for feeding solid oxide fuel cells where methane-containing synthesis gas is preferred.

In addition, a highly active and stable catalyst is desired for more efficient reforming at low temperatures. Rhodium has been found to be one of the most suitable metals for steam reforming [7, 8], and irreducible-oxides (γ -Al₂O₃, MgO, etc.) are found to be suitable supports with high stability due to strong interactions with rhodium [9]. The addition of ceria can usually improve the activity and carbon resistance of reforming catalysts [10-13]. The promotional effects of ceria have been explained by its high oxygen storage capacity (OSC), high capability for H₂ uptake, and high steam and CO₂ adsorption [10, 14-17]. The addition of ceria has also been reported to increase the reducibility and dispersion of metals [18, 19]. Recently, our group has developed highly active and sulfur-tolerant ceria-alumina supported Rh-Ni catalysts for steam reforming of jet fuels containing sulfur [6]. The effects of ceria and nickel addition on catalytic behavior of catalysts have been investigated for steam reforming of propane [20]. Nonetheless, the effect of ceria loading remains to be clarified for a better fundamental understanding.

Consequently, the present work focuses on the effects of ceria loading on the surface chemical characteristics and catalytic activity of alumina-supported Rh catalysts for low-temperature steam reforming of propane. Propane was chosen as the probe molecule because it is a simple one for mimicking liquid hydrocarbons and is the dominant component in the commercially available liquefied propane gas (LPG), a widely-used residential fuel. Reforming tests were carried out over alumina supported Rh catalysts with different ceria loading (0-100 wt%) under the same conditions to compare their catalytic behaviors. Analytical characterization was conducted to evaluate the ceria-alumina and Rh-support interactions.

2. Experimental

2.1. Catalyst Preparation

High-purity reagent-grade $\text{Rh}(\text{NO}_3)_3$ acidic aqueous solution and $\text{Ce}(\text{NO}_3)_3$ salt were purchased from Aldrich Chemicals and used as received. $\gamma\text{-Al}_2\text{O}_3$ (144 m^2/g , Sasol PURALOX TH 100/150) was used as the alumina support (Al) and for preparing CeO_2 -modified alumina support (CeAl) by wet impregnation of $\text{Ce}(\text{NO}_3)_3$ aqueous solution followed by calcination at 550 °C. For the preparation of Rh catalysts, $\text{Rh}(\text{NO}_3)_3$ was wet-impregnated onto the Al support and the CeAl support with 2 wt% Rh metal loading, followed by drying at 100 °C overnight and then calcination at 550 °C. CeO_2 was obtained after calcination of $\text{Ce}(\text{NO}_3)_3$ at 550 °C. The catalysts prepared in this work were 2 wt% Rh/ Al_2O_3 , 2 wt% Rh/5 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$, 2 wt% Rh/10 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$, 2 wt% Rh/20 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$, 2 wt% Rh/50 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$, 2 wt% Rh/75 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$, and 2 wt% Rh/ CeO_2 , which are denoted as 2Rh/Al, 2Rh/5CeAl, 2Rh/10CeAl, 2Rh/20CeAl, 2Rh/50CeAl, 2Rh/75CeAl, and 2Rh/Ce, respectively. The corresponding supports are denoted as Al, 5CeAl, 10CeAl, 20CeAl, 50CeAl, 75CeAl, and Ce, respectively.

2.2. Reaction Conditions

Propane steam reforming was carried out in a fixed-bed flow reactor system, as described in the previous report [20]. Approximately 50 mg of catalyst with particle sizes of 45 - 63 μm diluted with 1.0 g of silicon carbide (SiC, Checker Industries Corporation, grade 0080, 150 - 180 μm) was placed between two layers of quartz wool in the center of a stainless steel reactor (O.D., 0.5 in; I.D., 0.37 in; Length, 23 in). The rest of the tube was packed with α -alumina beads (Saint-Gobain Ceramics &

Plastics, Inc. Denstone[®] 99, 1/8 in) to enhance mixing and reduce the dead volume. The reforming temperature was controlled by a temperature-programmable tube furnace. The flow rates of the gases (Ar, H₂ and propane) were controlled by mass flow controllers. An SRI 8610C gas chromatograph (GC) equipped with a Supelco Carboxen-1000 column (5 ft × 1/8 in) and a thermal conductivity detector was used for the on-line analysis of gas products including H₂, CH₄, CO, CO₂, C₃H₈ and other light hydrocarbons if present.

The catalyst was reduced in situ at 535 °C (at a heating rate of 8 °C/min) under a 20 mL/min hydrogen flow (UHP grade) for 30 min. To prevent initial carbon deposition, Ar (100 mL/min) and steam were introduced into the reactor for 5 min before propane was introduced. Water was fed via an HPLC pump through a preheater and then into the reactor. Steam-to-carbon molar ratio was maintained at 3.0. Two pressure sensors (Cooper Instruments, PTA 145) -- one at the inlet, while the other at the outlet -- monitored the pressures in the reactor system. Most of the water vapor in the gas products was condensed in a condenser maintained at room temperature. Then, a drierite bed was used to remove the residual water before the reformat gas was allowed to flow into the online GC analyzer. The reaction was terminated by keeping the Ar flow at 100 mL/min and switching off the propane and steam valves. The furnace was then opened and cooled quickly to below 100 °C within one hour.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the calcined catalysts were obtained on a Scintag (Thermo Scientific) PAD V Powder Diffractometer using Cu-K_α radiation ($\lambda = 0.154$ nm) operated at 30 mA and 35 KV with a scanning speed of

1 °/min. The diffractograms were analyzed using MDI JADE 8.0 software and the standard JCPDS files. The crystallite sizes of Al₂O₃ and CeO₂ were calculated using the Al₂O₃ (440) and CeO₂ (111) peaks by Scherrer equation, $t = 0.85\lambda/(\beta\cos\theta)$, where t is the crystallite size, λ is the wavelength of the radiation, β is the full-width at half maximum (FWHM) of the diffraction peak (in rad.) and θ is the half of the diffraction angle [21].

N₂ adsorption-desorption was carried out at liquid-N₂ temperature (-196 °C) with a Quantochrome Autosorb-1 analyzer to measure the BET (Brunauer-Emmett-Teller) surface area and pore volume. Each sample was degassed by heating at 200 °C under vacuum prior to the measurement.

Temperature-programmed reduction (TPR) was conducted using freshly calcined catalyst samples on a Micromeritics AutoChem 2910 TPR/TPD analyzer with 5% hydrogen in argon with a temperature ramp of 10 °C/min. Hydrogen pulse chemisorption was carried out on the same device to measure the dispersion of Rh on the catalysts. The Rh dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per surface Rh atom. The inverse of the dispersion data, 1/D, provides an estimation of the average metal particle size of the supported catalysts according to the literature [22].

XPS analysis was performed on a Kratos Analytical Axis Ultra using an X-ray source of monochromatic alumina (1486.6 eV) at 280 W, with pass energies of 80 eV (survey) and 20 eV (high-resolution) with step sizes of 0.5 and 0.1 eV, respectively. The catalyst powders were pressed into 5 × 5 mm 3M double-sided tape using a mortar and pestle and visualized by a stereomicroscope to ensure complete and uniform coverage. Prior to the analysis, oxide samples were dried overnight in an

oven at 120 °C under atmospheric pressure. After drying, all samples were immediately stored in a container, and mounted for analysis.

Sample height positions were set from an O 1s signal at 529 eV after changing the lateral coordinates such that the measured signals from the sample powders were maximized, thus minimizing any possible signal from the 3M double-sided tape. The 3M double-sided tape was measured independently, and the characteristic shape of the C 1s line was not found when compared with the C 1s line collected during sampling. As a reference, we used the C 1s signal of the adventitious carbon (carbon of any surface adsorbed), which we fixed at 285 eV. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) and spectrometer transmission function for the Kratos instrument to the integrated peak areas. These RSFs take into consideration the X-ray cross-section and average attenuation length and instrumental factors related to X-ray source position, sample position, and spectrometer position. The spectrometer transmission function was corrected to a NPL calibration standard for the particular pass energy, magnification lens, aperture and iris settings, and transmission function of the spectrometer. The average sampling depth set on the C 1s line from an alumina powder was 30 Å.

A survey scan was initially recorded for the sample to identify the elements present. Composition as well as chemical states were determined from the charge-corrected high resolution scans.

The surface image was obtained by SEM using Leo 1530 Field Emission Scanning Electron Microscope. Operating voltage was 3keV, 5 keV, 10 keV, and 20 keV depending on the charging status of the particles.

The surface elemental analysis was performed by Auger electron spectroscopy (AES) using Physical Electronics 670 field emission scanning Auger nanoprobe.

Beams of 5 keV, 5 nA and 3 keV, 10 nA were used depending on the charging status of the particles.

2.4. Calculations

Propane and steam conversion and selectivity to H₂, CH₄, CO and CO₂ were calculated as previously described in Ref. [20]. The propane and steam conversion rates were calculated as follows:

$$r(\text{C}_3\text{H}_8) = \text{Conv.}(\text{C}_3\text{H}_8) \times \text{Flow}(\text{C}_3\text{H}_8)/W_{\text{cat}} \quad (\text{mmol g}^{-1} \text{s}^{-1})$$

$$r(\text{H}_2\text{O}) = \text{Conv.}(\text{H}_2\text{O}) \times \text{Flow}(\text{H}_2\text{O})/W_{\text{cat}} \quad (\text{mmol g}^{-1} \text{s}^{-1})$$

The production rates for H₂, CH₄, CO and CO₂ were calculated by using Ar as an internal standard. On the basis of these results the partial pressure of each gas in effluent (C₃H₈, H₂O, H₂, CH₄, CO, CO₂, and Ar) was obtained. The equilibrium constant K for water-gas-shift reaction and methanation reaction was calculated by using thermodynamic data from CRC handbook of chemistry and physics [23]. The reaction quotient (Q) for water-gas-shift reaction and methanation reaction was calculated as follows:

$$\text{For reaction } \alpha A + \beta B \leftrightarrow \sigma S + \tau T, \quad Q = \frac{[S]^\sigma [T]^\tau}{[A]^\alpha [B]^\beta}, \text{ where } [S], [T], [A], \text{ and } [B] \text{ are}$$

the partial pressures of S, T, A, and B. When reaction reaches equilibrium, Q equals equilibrium constant K.

The turnover frequency (TOF) of a catalyst is defined as the number of reactant molecules converted to products over one active site per second, which truly reflects the activity level of available catalytically active sites on surface. In the present work, each exposed Rh metal atom on the surface is considered as an active site for propane conversion. For each monometallic Rh catalyst, after a given time on steam (i.e., upon reaching steady propane conversion), the TOF was calculated using the following formula:

$$\text{TOF}(\text{C}_3\text{H}_8) = \text{Conv.}(\text{C}_3\text{H}_8) \times \text{Flow}(\text{C}_3\text{H}_8) / (W_{\text{cat}} \times (\text{wt\% Rh}) \times D_{\text{Rh}} / M_{\text{Rh}}) \quad (\text{s}^{-1})$$

where D_{Rh} is the Rh dispersion for the catalyst and M_{Rh} is the Rh metal atomic weight.

3. Results and Discussion

3.1. Textural Properties

The N_2 adsorption isotherms for the catalysts with different CeO_2 loading and their corresponding supports are given in **Fig. 1**. According to BDDT (Brunauer, Deming, Deming, and Teller) classification [24], all supports and supported Rh catalysts exhibited a type IV isotherm with a type H1 hysteresis loop at the high relative pressure range. The type IV isotherm is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high relative pressure. The shapes of hysteresis loops have often been identified with specific pore structures. The type H1 is often associated with porous materials known to consist of agglomerates or compacts of approximately uniform spheres in fairly regular array [24].

The pore size distribution curves generated using the Barrett-Joyner-Halenda (BJH) method [25, 26] are given in **Fig. 2**. The Rh catalysts showed similar pore size distribution to those of their corresponding supports. The CeO_2 and 2Rh/Ce gave a narrow pore size distribution from 7 to 10 nm, and a single most probable pore diameter of 8 nm. The Al_2O_3 and 2Rh/Al gave a broad range of pore size distribution from 12 to 28 nm, and a single most probable pore diameter of 21 nm. The CeAl supports and 2Rh/CeAl catalysts with CeO_2 loadings less than 50 wt% showed a similar pore size distribution to those of the Al_2O_3 and 2Rh/Al. Beyond 50 wt% CeO_2 loading, the CeAl supports and 2Rh/CeAl catalysts clearly showed two most probable pore diameters at 8 and 21 nm, respectively.

Table 1 shows the physico-chemical properties of the catalysts with different CeO_2 loading and their corresponding supports. The $\gamma\text{-Al}_2\text{O}_3$ used has a surface area of $144 \text{ m}^2/\text{g}$ and a pore volume of $0.81 \text{ cm}^3/\text{g}$. The surface area and pore volume of CeO_2 -modified alumina support decreased with the increasing CeO_2 loading from 140

m^2/g and $0.79 \text{ cm}^3/\text{g}$ for 5CeAl to $121 \text{ m}^2/\text{g}$ and $0.63 \text{ cm}^3/\text{g}$ for 20CeAl. When CeO_2 loading exceeded 50 wt%, the surface area and pore volume decreased greatly to $89 \text{ m}^2/\text{g}$ and $0.32 \text{ cm}^3/\text{g}$ for 50CeAl. However further increasing CeO_2 loading beyond 50 wt% did not further decrease surface area and pore volume significantly. 50CeAl and 75CeAl showed similar surface areas and pore volumes compared to those of pure CeO_2 support ($83 \text{ m}^2/\text{g}$ and $0.25 \text{ cm}^3/\text{g}$). The 2 wt% Rh loaded has very limited effect on the surface area and pore volume of the support and the loaded Rh is dispersed on support surface, as expected from previous studies [27-29]. The decrease of surface area and pore volume with increasing CeO_2 loading for CeO_2 -modified alumina supported metal catalysts were also reported by others [19, 27, 30-32]. These changes in the surface area and pore volume per unit mass are due to a combination of several factors including the partial coating of Al_2O_3 surface by CeO_2 , the change in mass density, the interaction between Al_2O_3 and CeO_2 , and a partial blockage of the smaller pores in alumina by oxide additive [31, 33]. Especially when CeO_2 loading exceeds 50 wt% the surface of Al_2O_3 may be completely covered by CeO_2 , thus the surface area and pore volume of 50CeAl (2Rh/50CeAl) and 75CeAl (2Rh/75CeAl) are similar to those of CeO_2 (2Rh/Ce).

As shown in **Table 1**, the Rh metal dispersion over alumina support was 45%. With the addition of 5 wt% to 20 wt% ceria to alumina support, the Rh dispersion slightly increased from 46 wt% to 49 wt%. The small increase of Rh dispersion with ceria addition is consistent with the data reported by De Rogatis et al. [27] and Cuauhtémoc et al. [34]. However further increasing CeO_2 loading beyond 20 wt% did not increase Rh dispersion any further. According to the well-known assumption $d = 1/\text{Dispersion}$ (nm) [22], the Rh particle size for 2Rh/CeAl catalysts with different CeO_2 loading were estimated to be between 2.0 and 2.2 nm.

3.2. XRD

Fig. 3 presents the XRD patterns of CeAl supports with different CeO₂ loading. The major phase of γ -Al₂O₃ was detected for the alumina support. With the increasing ceria addition, the XRD peak intensity for γ -Al₂O₃ phase significantly decreased and the peaks of the CeO₂ phase became more pronounced. Some reflections of CeO₂ phase even overlapped with those of the γ -Al₂O₃ phase. It has been reported [35] that the appearance of CeO₂ bulk in XRD is at CeO₂ loading of greater than 6 wt.% CeO₂/Al₂O₃, which is consistent with the results here. With more than 50 wt% ceria addition the γ -Al₂O₃ phase was almost undetectable by XRD. This is likely due to a segregation of ceria on the γ -Al₂O₃ surface or a formation of CeO₂ conglomerates covering γ -Al₂O₃ phase, which is consistent with the decrease of surface area shown in **Table 1**.

The XRD patterns of 2Rh/CeAl catalysts with different CeO₂ loadings are shown in **Fig. 4**. For all catalysts, phases related to the presence of Rh species could not be identified, which is due to the low Rh loading at relatively high dispersion. Metal species are also undetectable by XRD in 1 wt%Rh/Ce_{0.2}Zr_{0.8}O₂-Al₂O₃ [27], 1 wt%Rh/Al₂O₃ [27], Ni(5)Rh(1)/CeO₂ [36], and 3.5 wt%Rh/CeO₂/Al₂O₃ [37] catalysts. These results indicate that nanoparticles of RhO_x (< 5 nm) were present in the calcined catalysts, which is largely undetectable by XRD [38]. This is consistent with the Rh particle size estimated from dispersion data for the reduced catalysts.

The crystallite sizes of CeO₂ and Al₂O₃ calculated from the Scherrer equation for 2Rh/CeAl catalysts and corresponding supports are listed in **Table 1**. The crystallite size of CeO₂ and Al₂O₃ calculated from CeO₂ (111) and Al₂O₃ (440) reflection for CeAl supports was about 9 nm and 6 nm, respectively. These results indicate the

presence of segregated CeO₂ particles or their conglomerates on Al₂O₃ surface. The addition of Rh did not affect the crystallite size of CeO₂ and Al₂O₃.

3.3. TPR

Fig. 5 shows TPR profiles for CeO₂-Al₂O₃ supports with different CeO₂ loading. When 5 wt% or 10 wt% CeO₂ was loaded, only one broad peak around 550 °C can be observed. When 20 wt% CeO₂ was loaded, the broad peak started to split and a peak began to appear at lower temperature (ca. 410 °C). When the CeO₂ loading exceeded 20 wt%, the two peaks became clearly visible but with considerable overlap between them and the resolution was unclear. According to Vincent et al. [39], the first TPR peak corresponds to the creation of one layer of Ce³⁺ ions at the surface of the ceria, the second peak to an expanded cubic CeO_{2-x} phase derived from the initial ceria by a dilatation of the whole structure. Yao and Yao [35] reported two peaks at 500 and 750 °C for pure CeO₂ and a third peak at 850 °C for alumina-supported ceria; they ascribed the first to the reduction of surface capping oxygen, the second to the reduction of bulk oxygen anions, and the third to the reduction of the shared oxygen anions at the interface, respectively.

As shown in **Fig. 5**, the two peaks for pure CeO₂ appeared at 384 and 507 °C. With 75 wt% CeO₂ loaded on Al₂O₃ the two peaks shifted to 397 and 521 °C. With 50 wt% CeO₂ loaded on Al₂O₃ the first peak shifted to 410 °C and the second peak shifted to 550 °C or higher. These results indicate that the interaction between CeO₂ and Al₂O₃ makes CeO₂ more difficult to reduce than pure CeO₂ and the lower the CeO₂ loading, the more difficult for CeO₂ to reduce.

Fig. 6 shows TPR profiles of 2Rh/CeAl catalysts with different CeO₂ loadings. 2Rh/Al catalyst showed one reduction peak at ca. 176 °C, which is attributed to the

complete reduction of Rh_2O_3 . With the addition of 5 wt% ceria, the reduction peak became sharper and shifted to lower temperature (113 °C). The shift indicates that the reduction of Rh_2O_3 became easier upon ceria addition. With the addition of 10 wt% ceria, the reduction peak shifted to even lower temperature (94 °C). Damyanova et al. [30] also reported that the reduction peak for platinum oxide species shifts to lower temperature with increasing CeO_2 content from 0.5 to 3 wt%. However, beyond 20 wt% ceria, the first peak shifted to higher temperature with further increasing ceria loading. Moreover, the H_2 uptake calculated from the first reduction peak area was much higher than that corresponding to a 100% reduction of Rh_2O_3 , suggesting that some part of ceria also contribute to the first reduction peak. Below 20wt%, ceria was dispersed very well on alumina surface and each CeO_2 particle created an interfacial region with alumina. The area of this ceria-alumina interfacial region increased with increasing ceria loading (below 20 wt%) and more Rh was loaded on the ceria-alumina interfacial region promoting Rh-ceria-alumina interaction. Beyond 50 wt%, the alumina surface becomes covered by conglomerates of ceria particles, and the surface of CeAl was more like that of ceria.

A second peak started to appear for 2Rh/50CeAl at 294 °C, and shifted to lower temperature with increasing ceria content. The second peak could be assigned to the reduction of segregated CeO_2 particles or CeO_2 conglomerates. This means the existence of Al_2O_3 made CeO_2 more difficult to reduce, which is in agreement with the observations on the CeAl supports. The comparison of TPR profiles between 2Rh/CeAl catalysts and corresponding supports also suggests that loading rhodium onto CeAl supports enhances the reduction of CeO_2 . This is consistent with other studies, which have shown that the presence of noble metals causes easier reduction of the surface of CeO_2 [30, 35, 40, 41].

Table 2 presents the total H₂ uptake (mmol), Rh reduction degree and ceria reduction degree calculated from TPR data. The ceria reduction degree for 2Rh/20CeAl and 20CeAl was 32% and 29%, respectively, which is the highest among the 2Rh/CeAl catalysts and CeAl supports. The reduction degree for 2Rh/CeAl catalysts was slightly higher than that for corresponding CeAl supports, indicating that loading rhodium onto CeAl supports promotes CeO₂ reduction.

3.4. XPS Analysis

3.4.1 Ce 3d XPS

XPS spectra of Ce 3d for CeAl supports with different CeO₂ loading are shown in **Fig. 7**. The labels used in identifying Ce 3d XPS peaks in **Fig. 7** were established by Burroughs et al. [42], where V and U indicate the spin-orbit coupling 3d_{5/2} and 3d_{3/2}, respectively. The peaks referred to as v, v'' and v''' are contributed by CeO₂, and assigned to a mixture of Ce IV (3d⁹4f²) O (2p⁴), Ce IV (3d⁹4f¹) O (2p⁵), and Ce IV (3d⁹4f⁰) O (2p⁶), respectively. The peaks v₀ and v' are assigned to a mixture of Ce III (3d⁹4f²) O (2p⁵) and Ce III (3d⁹4f¹) O (2p⁶), respectively. The same peak assignment is applied to u structures. Peak deconvolution is marked by grey line in **Fig. 7** and reveals contributions from various final states. The multiplet splitting, for example between u'' and v'' peaks, was reported as 18.7 eV [42], 18.3 eV [43], and 18 eV [44], in agreement with that in **Fig. 7** of 18.4 eV. The Ce III content can be determined from the relative intensity of the u₀, u', v₀, and v' peaks to the total spectral intensity [45, 46], using the following equation:

$$Ce(III)(\%) = \frac{100 \times (u_0 + u' + v_0 + v')}{\sum (u + v)}$$

Using this method the Ce (III) surface content was determined for 10CeAl, 20CeAl, 50CeAl, 75CeAl, and CeO₂ supports (**Table 3**). Due to low resolution the Ce (III)

surface content was not determined for 5CeAl support. According to **Table 3**, 20CeAl support shows the highest Ce (III) surface content. This means that 20CeAl shows the strongest interaction between CeO_2 and Al_2O_3 , which is consistent with the above TPR results.

XPS of Ce 3d for 2Rh/CeAl catalysts with different CeO_2 loading are shown in **Fig. 8**. The Ce (III) surface content for 2Rh/CeAl catalysts is listed in **Table 3** and is higher than that for corresponding CeAl supports. This means that the interaction between rhodium and ceria makes CeO_2 easier to reduce, which is consistent with TPR results. The binding energy (BE) of Ce $3d_{5/2}$ is the same for all CeAl supports and is identical to that of pure ceria of 882.1 ± 0.2 eV (**Table 3**). The BE of Ce $3d_{5/2}$ for 2Rh/50CeAl, 2Rh/75CeAl, and 2Rh/Ce is the same as that for the corresponding supports, but the BE of Ce $3d_{5/2}$ for 2Rh/5CeAl, 2Rh/10CeAl, and 2Rh/20CeAl is higher than that for the corresponding supports. Moreover, the BE of Ce $3d_{5/2}$ for 2Rh/5CeAl, 2Rh/10CeAl, and 2Rh/20CeAl increased with increasing ceria loading. It means a change in the coordination number of Ce atoms in 2Rh/CeAl catalysts with ceria loading less than 20 wt%, probably due to an interaction between ceria and rhodium. The 2Rh/20CeAl catalyst exhibits the strongest interaction between ceria and rhodium.

3.4.2 O 1s XPS

XPS of O 1s core electron levels for CeAl supports and the corresponding 2Rh/CeAl catalysts are shown in **Figs. 9** and **10**, respectively. The BE of O 1s core levels are summarized in **Table 3**. The spectrum of CeO_2 surface had a peak at 529.2 eV (**Fig. 9**), which can be attributed to the lattice oxygen in CeO_2 [44, 47]. A shoulder appeared on the high BE side (ca. 531.1 eV) which can be assigned to adsorbed

oxygen [44, 48] or to surface hydroxyl species and/or adsorbed water species on the surface [44, 47]. The O 1s spectrum of Al₂O₃ has only a single peak at 531.5 eV (**Fig. 9**). The O 1s spectra for all CeAl supports except 75CeAl showed one peak, which could be considered as a combination of the oxygen from Al₂O₃, CeO₂, and adsorbed oxygen. With increasing CeO₂ loading, the BE of O 1s for CeAl supports (**Table 3**) shifted to lower side, which means the contribution of the oxygen from CeO₂ increased, and that from Al₂O₃ decreased. Eventually the one O 1s peak split as shown in O 1s spectrum of 75CeAl where the peak at 529.3 eV could be assigned to the oxygen in CeO₂, and the shoulder at ca. 531.2 eV could be assigned to a combination of oxygen from Al₂O₃ and adsorbed oxygen.

After addition of rhodium into CeAl supports the BE of O 1s (**Table 3**) became insensitive to CeO₂ loading and stayed at ca. 531.3 eV for all catalysts except 2Rh/75CeAl and 2Rh/Ce. This suggests a new oxide species containing rhodium on the surface of these catalysts or the overlapping contributions from individual support as well as from Rh oxide species. The O 1s spectra (**Fig. 10**) for 2Rh/75CeAl and 2Rh/Ce are similar to those for 75CeAl and CeO₂, except that the high BE peak might include the contribution from Rh oxide species. The BE of O1s for 2Rh/CeAl catalysts shifted 0.1 - 0.3 eV compared to that for corresponding supports, which could be related to the dispersion of Rh components on the surface and to the interaction between them.

3.4.3 Al 2p XPS

XPS spectra of Al 2p core levels for CeAl supports and 2Rh/CeAl catalysts are shown on **Fig. 11** and **12**, respectively. The BE of Al 2p core levels are summarized in **Table 3**. The Al 2p spectrum of all alumina-containing samples showed one single

peak. The BE of Al 2p for Al_2O_3 was 74.8 eV, which is higher than the reported value of 74 ± 0.2 eV [44]. With the addition of 5 wt% CeO_2 , the BE of Al 2p decreased to 74.3 eV and remained the same with increasing of ceria loading to 50 wt%. The BE of Al 2p for 75CeAl was 74.7 eV, which is close to that for Al_2O_3 . As suggested by Damyanova et al. [44], at low ceria loading a high dispersion of the cerium oxide species facilitates the formation of CeAlO_3 . This seemed the case for the supports with ceria loading less than 50wt%. With increasing ceria loading to 75 wt%, the ceria particle size increased and might make the formation of CeAlO_3 difficult due to a diffusion limitation of Ce to form solid solution with alumina.

The BE of Al 2p for 2Rh/Al was 74.5 eV and was identical to that for catalysts with ceria loading less than 50 wt%. Again this might reveal a new oxide species containing rhodium on the surface of these catalysts or result from the interaction between rhodium and interfacial CeAlO_3 . The BE of Al 2p for 2Rh/CeAl catalysts shifted 0.1 - 0.3 eV compared to that for corresponding supports, which could be connected with the interaction between the dispersed Rh and the support.

3.4.4 Rh 3d XPS

The Rh 3d XP spectra of 2Rh/CeAl catalysts with different ceria loadings are shown in **Fig. 13**, and the BE of Rh $3d_{5/2}$ are listed in **Table 3**. The spectra of all catalysts showed a doublet centered at around 309 and 314 eV. The two peaks correspond to the binding energy of Rh $3d_{5/2}$ and Rh $3d_{3/2}$, respectively, with a spin-orbit coupling of about 5 eV. The BE of Rh $3d_{5/2}$ for 2Rh/Al was 309.8 eV. With increasing ceria loading, the BE of Rh $3d_{5/2}$ shifted to lower side. Especially with increasing ceria loading from 50 wt% to 75 wt%, the BE of Rh $3d_{5/2}$ decreased significantly from 309.5 to 309.1 eV which was close to that of 309.0 eV for 2Rh/Ce.

This might indicate that with the increasing ceria loading the interaction between rhodium and ceria increased while the interaction between rhodium and CeAlO_3 or Al_2O_3 decreased. With more than 50 wt% ceria loading a layer of ceria might completely cover the surface of Al_2O_3 , thus the interaction between rhodium and ceria plays a major role.

3.4.5 Surface Atomic Ratio of Ce/Al, Rh/Al, and Rh/Ce

The XPS atomic ratios of Ce/Al vs. bulk atomic ratios of Ce/Al for Rh/CeAl catalysts and corresponding supports are shown in **Fig. 14**. The XPS ratios of Ce/Al for CeAl supports increased linearly with increasing ceria loading to 20 wt%. Further increasing ceria loading beyond 20 wt% led to an abrupt increase of XPS Ce/Al ratios. The Ce/Al ratios for 2Rh/CeAl catalysts exhibited the same trend except that the Ce/Al ratios remained the same with ceria loading up to 20 wt%. With less than 20 wt% ceria loading the XPS ratios of Ce/Al were less than the bulk ratios of Ce/Al, indicating a strong interaction between ceria and alumina on the surface.

The XPS ratios of Rh/Al vs. bulk ratios of Rh/Al for Rh/CeAl catalysts are shown in **Fig. 15**. With less than 20 wt% ceria loading the XPS ratios of Rh/Al remained the same and close to the bulk ratios of Rh/Al. With more than 20 wt% ceria loading an abrupt increase of XPS Ce/Al ratios was observed. The XPS ratios of Rh/Ce vs. bulk ratios of Rh/Ce for Rh/CeAl catalysts are shown in **Fig. 16**. The XPS ratios of Rh/Ce remained the same with ceria loading less than 20 wt% and after that increased abruptly. Moreover, at ceria loading of less than 20 wt%, the XPS ratios of Rh/Ce were much higher than the bulk ratios of Rh/Ce, meaning a strong interaction between rhodium and cerium. The fact that the XPS ratios of Ce/Al, Rh/Al, and Rh/Ce

maintained the same for catalysts with ceria loading less than 20 wt% strongly suggests a new oxide species containing rhodium on the surface of these catalysts.

The breakpoint of the XPS ratios of Ce/Al, Rh/Al, and Rh/Ce occurred at about 20 wt% of CeO₂; this indicates a change in the dispersion of ceria. Below this point ceria is well dispersed on the alumina surface. Similar phenomena was observed and a breakpoint of 6 wt% of CeO₂ was reported [44]. Since XRD results showed the existence of ceria crystallites of ca. 10 nm with 5 wt% ceria loading, ceria is likely to be dispersed as conglomerates on the surface of the catalysts with ceria loading less than 20wt%. Beyond this point small ceria conglomerates might join together and form big ceria particles which behave more or less similar to the CeO₂ support.

3.5. FE-SEM and AES

Fig. 17 presents the field emission-SEM (FE-SEM) images of supported Rh catalysts and CeAl supports. The FE-SEM image of 2Rh/Al₂O₃ catalyst shown in **Fig. 17** looks almost identical to the alumina support alone. From the low magnification image of Al₂O₃ (not shown), the alumina particles resemble spheres with the size (diameter) of 10 - 60 µm. The Al₂O₃ spheres show a very unsmooth surface with some smaller, amorphous fragments attached. These fragments do not have particular shapes and sizes and were most likely alumina debris.

The FE-SEM images of 2Rh/CeAl catalysts shown in **Fig. 17** that contain 5 wt% to 75 wt% CeO₂ are very similar to those of the corresponding CeAl supports. With 5 wt% ceria loading, the surface of 5CeAl appears to be almost the same as that of the pure alumina support, and the cerium was undetectable by AES. Since the peak pore size of the alumina support was around 21 nm (**Fig. 2**), the smaller CeO₂ nano-particles of less than 21 nm might “hide” in the pores of alumina and thus would

be invisible. On the surface of 10CeAl some white “dots” began to appear but still not very clear. With 10 wt% ceria loading the CeO_2 particles became larger and might grow out of the pores of alumina and start to appear on the external surface. On the surface of 20CeAl the white “dots” became clearly visible, as shown in **Fig. 17**. These white “dots” are CeO_2 particles, with the size of 100 - 200 nm dispersed on the alumina surface, as confirmed by AES described below.

AES analysis was performed on the two specific areas observed under SEM marked by 1 and 2, as shown in **Fig. 18** for the 2Rh/20CeAl sample. The area 1 has some white “dots” in it and the area 2 has not. As can be seen from AES spectra in **Fig. 18b**, area 1 had Ce signal while area 2 had not. This verified that the white “dots” on the surface of supports are indeed CeO_2 particles. The rhodium was undetectable on both areas due to the detection limit.

Another **image of 2Rh/20CeAl from side view** in **Fig. 17** revealed some interesting and important information. Some ceria particles seem to be buried under amorphous alumina. Each ceria particle created an interfacial region with alumina, the area of which depended on the number and size of ceria particles. A large interfacial region indicates a strong interaction between ceria and alumina. With ceria loading below 20 wt% the surface area decrease was most possibly caused by the coating of alumina pore structure due to the growth of ceria particles. Due to pore size limitation of the alumina support (**Fig. 2**), the CeO_2 inside the pore channels of Al_2O_3 most likely exists as nano particles smaller than 21 nm.

On the surface of 50CeAl (**Fig. 17**), the CeO_2 particles became more numerous and increase in size to between 200 - 300 nm. Some CeO_2 particles even formed big areas of conglomerates covering the alumina surface. With 75 wt% ceria loading, the surface of 75CeAl (**Fig. 17**) were completely covered by a layer of CeO_2 particles,

some of which combined together and formed particles with size of more than 500 nm. The low magnification image of 75CeAl and AES analysis showed flake-like CeO₂ particles with size comparable to that of pure ceria particles. During the preparation of 75CeAl, some excessive cerium was not loaded onto the alumina surface and later became isolated CeO₂ particles. Some ceria particles on the surface of alumina may also grow bigger and separate from the alumina surface. In general, with ceria loading of more than 50 wt%, the surface of CeAl was more like that of ceria, therefore the surface areas of 50CeAl and 75CeAl were close to that of ceria.

The low magnification image of CeO₂ showed that the ceria particles are flake-like and with the size of 10 - 40 μ m. There were also some small fragments on the surface of CeO₂, which were most likely ceria debris (not shown).

3.6. Catalytic Behavior of 2Rh/CeAl Catalysts

Fig. 19 shows the conversion profiles of steam reforming of propane over 2Rh/CeAl catalysts at 500 °C by using 0.05 g catalyst and Ar as dilute gas. At 500 °C, 2Rh/20CeAl catalyst showed the highest C₃H₈ conversion (100%), followed by 2Rh/10CeAl (96%), 2Rh/5CeAl (95%), 2Rh/50CeAl (88%), 2Rh/75CeAl (84%), 2Rh/Al (81%) and 2Rh/Ce (56%) catalysts. For all catalysts the conversions of C₃H₈ at 500 °C kept almost the same as the initial conversion within 11 hours on stream. At 500 °C, 2Rh/20CeAl catalyst showed the highest H₂O conversion (37%). 2Rh/10CeAl, 2Rh/5CeAl, 2Rh/50CeAl, and 2Rh/75CeAl catalysts showed similar H₂O conversion (33%), and 2Rh/Al and 2Rh/Ce catalysts showed similar H₂O conversion (around 28%).

The product distributions over 2Rh/CeAl catalysts at 500 °C are presented in **Table 4**. 2Rh/Al catalyst showed the lowest H₂ content (60.7), and H₂ content

increased with the increasing ceria loading. 2Rh/Al catalyst showed the highest CO content (7.9%), and CO content decreased to 3.9% with 5 wt% ceria loading and kept almost the same for the remaining catalysts. CH₄ content increased from 14.0% to 16.4% with addition of 5 wt% ceria and then decreased with further increasing of ceria loading to 10.9% for 2Rh/75CeAl. 2Rh/Ce showed the lowest CH₄ content of 4.6%. 2Rh/Ce catalyst showed the highest CO₂ content (20.3%), 2Rh/Al catalyst showed the lowest CO₂ content (16.6%), while all other catalysts showed similar CO₂ content (19.5%). These results suggest that CeO₂-modified alumina supported Rh catalysts can greatly reduce CO content and increase CO₂ content.

By comparing the reaction quotient and reaction equilibrium constant shown in **Table 5**, we can see that over all catalysts except 2Rh/Al, water-gas-shift reaction reached equilibrium. This again indicates that adding CeO₂ to alumina support can greatly promote the oxidation of CO, thus facilitate water-gas-shift reaction. Ceria has been reported to promote supported metal catalysts for the water-gas-shift reaction [49-51], and CO oxidation [52, 53], which is consistent with current results. It can also be seen from **Table 5** that over 2Rh/20CeAl catalyst methanation reaction reached equilibrium.

4. Discussion

4.1. Influence of Ceria Loading

In the previous study [20] we found that ceria addition onto alumina supported Rh catalyst greatly increased the propane reforming rates by lowering the activation energy and enhancing the steam and propane adsorption. In this study, 2Rh/20CeAl showed the highest propane conversion rate and turnover frequency among the alumina supported Rh catalysts with different CeO₂ loadings (**Fig. 20**). Ceria loading

of 20 wt% was observed as a breaking point in BET, TPR, and XPS analysis. Adjusting loading levels of ceria can change the nanostructures of active phases and create catalytically more active sites. It is worth noting that for the practical use in the automotive exhaust treatment system, the ceria loading is also about 20% with respect to alumina [35]. The effects of CeO_2 loading on the catalytic behaviors of Al_2O_3 or ZrO_2 supported metal catalysts were investigated by others and different optimal ceria loadings were reported [13, 30, 31].

Previously we proposed that the loaded ceria may exist as a segregation of ceria or ceria conglomerates on alumina surface [20]. The FE-SEM results in this study clearly confirmed this. Moreover, the dispersion of ceria on alumina surface was greatly affected by ceria loading. For loading of 5, 10, and 20 wt% ceria was dispersed very well on alumina surface and each CeO_2 particle created an interfacial region with alumina. Below 20 wt%, the area of this ceria-alumina interfacial region increased with increasing of ceria loading, and each CeO_2 particle strongly interacted with alumina. Further increasing ceria loading beyond 50 wt%, the ceria-alumina interfacial region diminished as ceria formed big areas of conglomerates covering the alumina surface.

4.2. Interaction between Rh and Support

As shown in TPR results, ceria addition to alumina supported Rh catalysts made both rhodium oxide and cerium oxide easier to reduce. This suggests strong interaction between Rh and CeO_2 . XPS analysis showed a constant ratio of Rh : Ce : Al for catalysts with ceria loading less than 20 wt%, indicating strong interaction between rhodium, ceria, and alumina. Such strong interaction might favor the formation of new oxide species containing Rh, Ce, and Al. On the basis of the above

results and analysis, it is highly possible that rhodium was loaded onto the interfacial region of ceria-alumina. A possible model for 2Rh/20CeAl catalyst was proposed, as shown in **Fig. 21**. This model is a modification to the previously proposed model [20] in that rhodium stays at the interface of ceria and alumina and the relative size of CeO_x to Rh is closer to that of the real catalyst. In this model, $\text{CeO}_x\text{-Al}_2\text{O}_3$ interfacial region provides sites for steam adsorption and activation and rhodium provides sites for propane adsorption and activation. An increase in the ceria-alumina interface area helps to increase Rh dispersion as shown by H_2 chemisorption data and create strong interaction between Rh and support.

5. Conclusions

The influence of ceria loading on alumina supported Rh catalyst for steam reforming of propane has been studied. With the addition of ceria, the catalytic activity of Rh catalyst for propane reforming can be greatly improved. The Rh catalyst supported on 20 wt% $\text{CeO}_2\text{-Al}_2\text{O}_3$ showed the highest activity. TPR characterization shows that the interaction between Rh and ceria makes both rhodium oxide and ceria easier to reduce. XPS analysis indicates strong interaction between ceria and alumina in 20CeAl supports and strong interaction between Rh and support in 2Rh/20CeAl catalyst. FE-SEM reveals that ceria is highly dispersed as separate nanoparticles on the surface of alumina at CeO_2 loading of 20 wt%, and ceria particles form big area of conglomerates covering alumina surface at high CeO_2 loading (≥ 50 wt%). By combining the characterization and catalytic tests, it has become clear that Rh interacting with the interfacial region of CeO_2 and Al_2O_3 is more active than Rh on CeO_2 alone or Al_2O_3 alone. The 2Rh/20CeAl catalyst showed the highest activity for propane steam reforming at 500 °C, possibly because of its

high Rh and ceria dispersion, high reducibility of ceria and rhodium oxide, and strong interaction between Rh, ceria, and alumina.

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A

B

Fig. 1. BET isotherm for 2Rh/CeAl catalysts A and corresponding supports B.

A

B

Fig. 2. Pore size distribution for 2Rh/CeAl catalysts A and corresponding supports B.

Fig. 3. XRD patterns of CeO₂-Al₂O₃ supports with different CeO₂ content.

Fig. 4. XRD patterns of 2Rh/CeAl catalysts with different CeO_2 content.

Fig. 5. TPR profiles of CeO_2 - Al_2O_3 supports with different CeO_2 content.

Fig. 6. TPR profiles of 2Rh/CeAl catalysts with different CeO_2 content.

Fig. 7. XPS of Ce 3d for CeO_2 - Al_2O_3 supports with different CeO_2 content.

Fig. 8. XPS of Ce 3d for 2Rh/CeAl catalysts with different CeO₂ content.

Fig. 9. XPS of O 1s for CeO₂-Al₂O₃ supports with different CeO₂ content.

Fig. 10. XPS of O 1s for 2Rh/CeAl catalysts with different CeO₂ content.

Fig. 11. XPS of Al 2p for CeO_2 - Al_2O_3 supports with different CeO_2 content.

Fig. 12. XPS of Al 2p for 2Rh/CeAl catalysts with different CeO₂ content.

Fig. 13. XPS of Rh 3d for 2Rh/CeAl catalysts with different CeO₂ content.

Fig. 14. XPS Ce/Al ratios as a function of the bulk Ce/Al ratio for 2Rh/CeAl catalysts and corresponding supports.

Fig. 15. XPS Rh/Al ratios as a function of the bulk Rh/Al ratio for 2Rh/CeAl catalysts.

Fig. 16. XPS Rh/Ce ratios as a function of the bulk Rh/Ce ratio for 2Rh/CeAl catalysts.

Fig. 17. Field emission-scanning electron microscopy (FE-SEM) images of Rh catalysts loaded on CeAl supports

Fig. 18. Auger electron spectra of 2Rh/20CeAl catalyst where spectra 1 and 2 (**Left**) correspond to area 1 and area 2 marked in SEM image (**Right**).

Fig. 19. The conversion profiles of steam reforming of propane over 2Rh/CeAl catalysts. Conditions: catalyst, 0.05 g, silicon carbide, 1.00 g; Ar: 100 mL/min; C₃H₈, 12.5 mL/min; H₂O, 0.09 mL/min; S/C = 3; WHSV(C₃H₈) = 15,000 mL/(gcat·h).

Fig. 20. C_3H_8 reaction rate and turnover frequency as a function of CeO_2 loading at 500°C .

Fig. 21. Possible model for 2Rh/20CeAl catalyst during steam reforming of propane.

Table 1. Physical properties of 2Rh/CeAl catalysts and corresponding supports

Sample	BET surface (m ² /g)	Pore volume (mL/g)	Rh dispersion ^a (%)	Rh particle size ^b (nm)	CeO ₂ crystallite size (nm) ^c	Al ₂ O ₃ crystallite size (nm) ^c
2Rh/Al	148	0.77	45	2.2	-	6.4 ± 0.3
2Rh/5CeAl	140	0.70	46	2.2	9.8 ± 0.8	6.5 ± 0.4
2Rh/10CeAl	129	0.60	48	2.1	9.0 ± 0.4	6.6 ± 0.5
2Rh/20CeAl	117	0.57	49	2.0	8.8 ± 0.4	7.3 ± 0.7
2Rh/50CeAl	91	0.30	46	2.2	8.8 ± 0.3	-
2Rh/75CeAl	93	0.24	48	2.0	8.3 ± 0.3	-
2Rh/Ce ^d	92	0.24	45	2.2	9.1 ± 0.3	-
γ-Al ₂ O ₃	144	0.81	-		-	6.8 ± 0.3
5CeAl	140	0.79	-		9.7 ± 0.9	6.1 ± 0.4
10CeAl	123	0.71	-		9.4 ± 0.5	6.7 ± 0.4
20CeAl	121	0.63	-		8.4 ± 0.4	6.9 ± 0.6
50CeAl	89	0.32	-		8.3 ± 0.3	-
75CeAl	85	0.27	-		8.5 ± 0.3	-
CeO ₂ ^d	83	0.25	-		9.2 ± 3	-

^a Measured by H₂ chemisorption.^b The metal particle size (*d*) was calculated from the equation $d = 1/Dispersion$ (nm) according to literature.[22]^c Calculated from CeO₂ (111) and Al₂O₃ (440) reflection employing Scherrer equation, respectively.^d CeO₂ was obtained after calcination of Ce(NO₃)₃ at 550 °C.

Table 2. TPR data of 2Rh/CeAl catalysts and corresponding supports^a

Sample	Total H ₂ uptake (mmol)	Rh reduction degree (%)	CeO ₂ reduction degree (%)
2Rh/Al	0.087	100	-
2Rh/5CeAl	0.098	100	25
2Rh/10CeAl	0.105	100	21
2Rh/20CeAl	0.143	100	32
2Rh/50CeAl	0.197	100	25
2Rh/75CeAl	0.242	100	24
2Rh/Ce	0.247	100	18
γ -Al ₂ O ₃	-	-	-
5CeAl	0.010	-	23
10CeAl	0.017	-	20
20CeAl	0.050	-	29
50CeAl	0.096	-	22
75CeAl	0.140	-	21
CeO ₂	0.152	-	17

^a The weight used for TPR experiment for each sample was ca. 0.30 g.

Table 3. XPS parameters of 2Rh/CeAl catalysts and corresponding supports

Sample	BE (eV)				Ce (III) Surface Content / %
	Rh 3d _{5/2}	O 1s	Al 2p	Ce 3d _{5/2}	
2Rh/Al	309.8	531.3	74.5	-	-
2Rh/5CeAl	309.7	531.3	74.5	882.3	-
2Rh/10CeAl	309.7	531.4	74.5	882.4	9.1
2Rh/20CeAl	309.6	531.3	74.5	882.6	21.4
2Rh/50CeAl	309.5	531.2	74.6	882.1	16.4
2Rh/75CeAl	309.1	531.3 ^a , 529.3 ^b , 531.3 ^c	74.8	882.2	13.4
2Rh/Ce	309.0	529.3 ^b , 531.3 ^c	-	882.2	11.3
γ -Al ₂ O ₃	-	531.5	74.8	-	-
5CeAl	-	531.2	74.3	882.1	-
10CeAl	-	531.1	74.3	882.2	7.7
20CeAl	-	531.1	74.4	882.0	13.1
50CeAl	-	531.0	74.3	881.9	8.2
75CeAl	-	531.4 ^a , 529.3 ^b , 531.1 ^c	74.7	882.2	9.7
CeO ₂	-	529.2 ^b , 531.1 ^c	-	882.1	10.8

^a From Al₂O₃, ^b From CeO₂, ^c From adsorbed oxygen

Table 4. Product distribution over 2Rh/CeAl catalysts at 500 °C

Catalyst	H ₂ (%)	CO (%)	CH ₄ (%)	CO ₂ (%)
2Rh/Al	60.7 ± 0.3	7.9 ± 0.4	14.0 ± 0.4	16.6 ± 0.3
2Rh/5CeAl	60.8 ± 0.3	3.9 ± 0.1	16.4 ± 0.4	18.8 ± 0.1
2Rh/10CeAl	61.6 ± 0.3	3.3 ± 0.2	15.4 ± 0.5	19.4 ± 0.2
2Rh/20CeAl	63.9 ± 0.3	3.3 ± 0.1	13.3 ± 0.4	19.5 ± 0.3
2Rh/50CeAl	64.7 ± 0.3	3.3 ± 0.4	12.4 ± 0.1	19.5 ± 0.4
2Rh/75CeAl	66.8 ± 0.2	3.4 ± 0.2	10.9 ± 0.5	19.5 ± 0.2
2Rh/Ce	71.8 ± 0.2	3.3 ± 0.4	4.6 ± 0.2	20.3 ± 0.2

Table 5. The reaction quotient (Q^a) over 2Rh/CeAl catalysts at 500 °C

Catalyst	$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$
	5.92 ^b	74.22 ^b
2Rh/Ce	5.4±0.3	18±1
2Rh/75CeAl	6.0±0.7	36±2
2Rh/50CeAl	6.3±0.6	50±2
2Rh/20CeAl	6.5±0.3	72±2
2Rh/10CeAl	5.7±0.4	42±2
2Rh/5CeAl	4.4±0.3	40±2
2Rh/Al	1.9±0.2	29±2

^a For reaction $\alpha A + \beta B \leftrightarrow \sigma S + \tau T$, $Q = \frac{[S]^\sigma [T]^\tau}{[A]^\alpha [B]^\beta}$, where [S], [T], [A], and [B] are the partial pressures of S, T, A, and B. When reaction reaches equilibrium, Q equals equilibrium constant K.

^b The reaction equilibrium constant K at 500 °C.