Hydrogen production from oxidative steam reforming of ethanol over rhodium catalysts supported on Ce–La solid solution

Xue Han, Yunbo Yu*, Hong He*, Wenpo Shan
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

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ABSTRACT
The catalytic behaviors of Rh catalysts supported on Ce–La solid solution in H2 production from the oxidative steam reforming (OSR) of ethanol were studied for the first time. 1%Rh/Ce0.7La0.3Oexhibits 100% ethanol conversion at 573 K with H2 yield rate 214 μmol g-cat−1 s−1/C01, which is 150 K lower than that required for comparable performance with 1%Rh/CeO2. La doping also enhanced the stability by accelerating CH3COCH3 conversion and gave low CO selectivity due to the high water gas shift activity. X-ray diffraction and Raman spectroscopy characterizations indicate the formation of Ce–La solid solutions and oxygen vacancies. H2 temperature-programmed reduction and thermo-gravimetric measurement results confirmed that the redox properties of Rh/CeO2 were greatly enhanced by La doping, which accelerated ethanol conversion, promoted H2 yield, and maintained good long-term activity for the OSR reaction.

1. Introduction
Producing hydrogen from the catalytic reforming of bioethanol has recently attracted increasing attention, as a promising way to replace fossil fuels with sustainable energy sources [1–5]. Because of its high H2 yield, steam reforming of ethanol over supported metal has been studied extensively in recent years [6–8]. However, it is a highly endothermic reaction, typically operating within the temperature range of 700–1000 K [9,10]. This highly reforming temperature also favors the reverse water-gas shift (R-WGS) reaction (CO2 + H2 ↔ CO + H2O) and thus the generation of CO [11], the presence of which degrades the performance of Pt electrodes in fuel cell systems [12]. To avoid such a disadvantage, operating the reforming process at lower temperature is a good choice. However, low temperature reforming usually decreases the conversion of ethanol and increases the formation of undesired by-products such as CH2=CH2 and CH3COCH3, which can easily convert to coke deposits and result in catalyst deactivation [4]. Therefore, reducing the undesired by-products is a very important issue in low-temperature hydrogen production. It has been reported that the introduction of molecular oxygen in the reaction stream (Oxidative steam reforming, OSR) provides advantages such as depression of coke formation and transformation of undesired partial oxidation by-products into more stable products (H2, CO2, and CH4), and also exhibits high ethanol conversion and H2 yield, and low CO selectivity at low temperature [13–15].

* Corresponding authors. Tel./fax: + 86 10 62849123.
E-mail addresses: ybyu@rcees.ac.cn (Y. Yu), honghe@rcees.ac.cn (H. He).
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For the OSR process, thermodynamic calculation studies have indicated that as temperature is raised, \( \mathrm{H}_2 \) and \( \mathrm{CO} \) concentrations increase, whereas those of \( \mathrm{CO}_2 \) and \( \mathrm{CH}_4 \) as well as the thermodynamically unstable by-products (e.g. \( \mathrm{CH}_2\mathrm{CHO} \) and \( \mathrm{CH}_3\mathrm{COCH}_3, \mathrm{CH}_2\mathrm{CH}_2 \)) decrease [4,16]. The distributions of hydrogen production at low temperatures due to its superior the most active component for ethanol conversion and selection of catalyst[4,5].

Numerous studies have demonstrated that Rh is generally the most active component for ethanol conversion and hydrogen production at low temperatures due to its superior C–C bond cleavage ability [4,5,17,18]. Meanwhile, the production of \( \mathrm{H}_2 \) from ethanol reforming is very sensitive to the nature of the support, as has been experimentally verified [19–21]. Recently, \( \mathrm{CeO}_2 \) has extensively been utilized as a support for hydrogen production from ethanol mainly because of the following reasons: 1) it favors ethanol dehydrogenation to \( \mathrm{CH}_2\mathrm{CHO} \) rather than dehydration to \( \mathrm{CH}_2\mathrm{CH}_2 \) (ethylene is easily polymerizable to coke) [17,19]; 2) ceria enriched with oxygen vacancies, by creating a strong metal-support interaction, promotes the dispersion of noble metals, and thus the activity for ethanol reforming [11,22]; 3) its remarkable oxygen-storage/release capacity (OSC) and high oxygen mobility, allowing gasification/oxidation of deposited carbon as soon as it forms, improves the catalyst stability [10]; 4) ceria-supported noble metal is active for the water gas shift reaction [23,24].

All of the above make \( \text{Rh/CeO}_2 \) a good candidate for ethanol reforming, and much work has been carried out on its further improvement. For example, a second metal such as Ni, Pd or Pt was loaded together with Rh to enhance the \( \text{H—H} \) bond dissociation and improve catalytic activity [25–27]; while doping ions such as \( \text{Zr}^{4+} \) were introduced to make a solid solution with several improved catalytic properties compared to \( \text{Rh/CeO}_2 \) [28]. However, to achieve its wide industrial application in hydrogen production from ethanol, more effort is still needed. For example, at low temperature, ethanol conversion and hydrogen yield still need to be further improved; while \( \text{CO} \), unstable by-products and coke deposition also need to be greatly lowered.

In other catalytic applications, La has been introduced to promote the activity and/or stability of ceria-based catalysts. Reddy et al. argued that \( \text{La}^{3+} \) doping greatly increased the OSC value of ceria because more oxygen vacancies were created by substitution of \( \text{Ce}^{4+} \) cations with \( \text{La}^{3+} \) cations, leading to high performance in \( \text{CO} \) oxidation [29]. Furthermore, a \( \text{Ce—La} \) solid solution has been reported by Bueno-Lopez et al. to be more active for soot oxidation than pure ceria [30]. La doping also enhanced the activity and stability against sintering of ceria-supported noble metal catalysts for the low-temperature water-gas shift reaction, giving an opportunity for lowering the concentration of \( \text{CO} \) in \( \text{H}_2 \) production [31,32].

Inspired by all of the above, we employed La-doped ceria as the support for OSR reaction catalysts. The supports with different molar ratios of \( \text{Ce/La} \) (\( \text{Ce}_{1-x}\text{La}_x\text{O}_y \), denoted as \( \text{CLy} \) hereafter, where \( x \) denotes the mol. % of \( \text{La} \) in the precursor) were prepared by urea co-precipitation [33]. By optimization of the ratio of \( \text{La}/\text{Ce} \), it was found that \( \text{La}^{3+} \)-doping greatly enhanced the ethanol conversion and \( \text{H}_2 \) yield during the low temperature OSR reaction. Introducing \( \text{La} \) into the ceria lattice markedly tunes the redox properties of \( \text{Rh/CeO}_2 \) catalyst, which may contribute to these enhancements for \( \text{H}_2 \) production from ethanol.

## 2. Experimental

### 2.1. Catalyst preparation

\( \text{Ce(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) and \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) were used as precursors for the preparation of supports by urea co-precipitation with a varied \( \text{La}/(\text{Ce + La}) \) molar ratio (\( x \)). The precipitate was dried at 373 K for 12 h, and then was thermally treated in a furnace at 773 K for 5 h in air. The supported rhodium catalysts were prepared by impregnating the \( \text{CLx} \) materials in a solution of \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \), then drying at 373 K for 12 h, which was followed by calcination at 773 K for 3 h in air. Over the prepared catalysts, the rhodium loading was 1 wt. %.

### 2.2. Catalyst characterization

The BET (Brunauer, Emmett, and Teller) surface areas of catalysts were determined on Autosorb iQ-1MP automatic equipment by physical adsorption measurements with \( \text{N}_2 \) at 77 K. Prior to \( \text{N}_2 \) physical sorption, the samples were degassed at 573 K for 3 h. X-ray powder diffraction (XRD) patterns were measured using a PANalytical X’Pert Pro diffractometer with \( \text{Cu} \) \( \text{Kx} \) (\( \lambda = 0.15406 \text{ nm} \)) radiation. Data of 2\( \theta \) were collected from 10 to 90° with step size of 0.02°, and then the XRD results were refined by Rietveld analysis. X-ray photoelectron spectra (XPS) were recorded in a scanning X-ray microprobe (PHI Quantera, ULVAC—PHI, Inc) using Al \( \text{Kx} \) radiation. Binding energies were calibrated using the C 1s level (BE = 284.8 eV) as standard.

Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVR DLPC-DL-03). A continuous diode-pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation and the power output was about 48 mW. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm\(^{-1}\). The diameter of the laser spot on the sample surface was focused at 25 \( \mu \text{m} \). The spectral resolution was 2.0 cm\(^{-1}\). All Raman spectra used in this paper were original and unsmoothed.

Hydrogen temperature-programmed reduction (\( \text{H}_2\)-TPR) measurements were carried out in a conventional set-up equipped with a mass spectrometer (HP20). Samples (100 mg) were heated from room temperature to 1173 K in a reducing gas mixture (5.2 vol. % \( \text{H}_2/\text{He} \), 30 mL/min) at a ramp rate of 10 K min\(^{-1}\). The OSC values were measured by the thermo-gravimetric (TG, STARe system METTLER TOLEDO) method. In this analysis, the sample was purged in Ar and then reduced in 5.2% \( \text{H}_2/\text{Ar} \) and oxidized in 10% \( \text{O}_2/\text{Ar} \) alternately at 673 K. Simultaneously, the weight change of the employed catalyst was measured with time on-stream.

The metallic phase dispersion of used catalysts was calculated from \( \text{H}_2 \) chemisorption. Experiments were performed at low temperature to limit the “spillover” phenomenon using a pulse chromatographic apparatus [34]. After using 2 h at 673 K under the OSR reaction conditions, the sample was
cooled to 223 K by liquid nitrogen. Pulses of hydrogen were injected until saturation was indicated by constant peak area of the final pulses. This permitted the evaluation of total hydrogen uptake \((H_{\text{in}})\). Subsequently, the catalyst was flushed for 10 min under Ar to remove the physically adsorbed hydrogen molecules, and hydrogen was pulsed again until saturation \((H_{\text{out}})\). The amount of chemisorbed hydrogen was calculated using \(H_{\text{C}} = H_{\text{C1}} - H_{\text{C2}}\).

2.3. Catalytic measurements

The OSR reaction of ethanol \((\text{EtOH})\) was carried out in a continuous-flow fixed-bed micro-reactor made of a quartz tube of 6 mm inner diameter with 100 ± 2 mg catalyst (40–60 mesh, diluted with 300 mg SiO\(_2\)). A mixture of ethanol and water was supplied by a syringe pump at a rate of 0.06 mL/min. After being sufficiently vaporized by passing through a preheating zone at 473 K, this mixture was continuously fed into the reactor together with the N\(_2\) carrier (300 mL/min) and O\(_2\) \((\text{EtOH}: \text{H}_2\text{O}: \text{O}_2 = 1: 3: 0.5)\), with a space velocity of 93 μmol g-cat\(^{-1}\) s\(^{-1}\). The catalytic reaction was tested from 473 K to 723 K at six evenly spaced temperature points and each point was held for at least 1.5 h. The effluent gases were analyzed on-line at a given temperature using a gas chromatograph (Shimadzu, GC-2014C) equipped with two TCDs and one FID on-line at a given temperature using a gas chromatograph. The contents of N\(_2\), CO, CO\(_2\), and CH\(_4\) were measured at the inlet and at the outlet of the reactor, respectively.

The selectivities to carbon containing products \((\text{EtOH}\), in and \(\text{EtOH}\), out\) represent the concentration of an adsorbed molecule \((X)\) before and after acetaldehyde addition, respectively.

\[
F_x = \frac{[X] \times F_{N_2}}{[N_2]} \quad (1)
\]

where \(F_{N_2}\) is N\(_2\) flow rate at room temperature, \([N_2]\) is the concentration of N\(_2\) (%), and \([X]\) is the concentration of X (%). Ethanol conversion was calculated according to equation (2) where \(F_{\text{EtOH}, \text{in}}\) and \(F_{\text{EtOH}, \text{out}}\) represent the normal flow rate of the ethanol measured at the inlet and at the outlet of the reactor, respectively.

\[
C_{\text{EtOH}} = \frac{F_{\text{EtOH}, \text{in}} - F_{\text{EtOH}, \text{out}}}{F_{\text{EtOH}, \text{in}}} \quad (2)
\]

The yields of \(X\) \((Y_x)\) were calculated by the following equation:

\[
Y_x = \frac{F_x}{F_{\text{EtOH}, \text{in}}} \quad (3)
\]

The selectivities to carbon containing products \((S_x)\) were calculated according to the following equation:

\[
S_x = \frac{F_x}{\alpha \times F_{\text{EtOH}, \text{in}} \times C_{\text{EtOH}}} \quad (4)
\]

where \(\alpha\) is the number of carbon atoms in the product (\(\alpha = 1\) for CO, CO\(_2\) and CH\(_2\)); while \(\alpha = 2\) for C\(_2\)H\(_4\) and CH\(_3\)CHO).

In this study, the catalyst stability test was carried out at 673 K in the same micro-reactor and under the same feeding conditions as the catalytic activity test.

To reveal the role of La doping in the transformation of CH\(_3\)CHO during the OSR reaction, 10% CH\(_3\)CHO (molar ratio of CH\(_3\)CHO: EtOH = 10%) was added to the feed mixture of the OSR reaction from 573 K to 723 K while keeping the space velocity and other reaction conditions unchanged. The changes of the yields of \(X\) after acetaldehyde addition were calculated by the following equation:

\[
d_x = \frac{F_x\text{after} - F_x\text{before}}{F_{\text{EtOH}, \text{in}}} \quad (5)
\]

Similarly, 10% acetone (molar ratio of CH\(_3\)COCH\(_3\); EtOH = 10%) was added to the OSR reaction mixture, and then the distribution of production was measured with 1% CO and 3% water (N\(_2\) balance). The space velocity was 93 μmol g-cat\(^{-1}\) s\(^{-1}\).

3. Results

3.1. OSR reaction

Ethanol conversion and H\(_2\) yield from each mole of ethanol at different temperatures are shown in Fig. 1. On the 1%Rh/\(\text{CeO}_2\) (Rh/C, \(x = 0\)) catalyst, ethanol conversion of 98% was obtained at 723 K, with H\(_2\) yield of 2.20 mol/mol\(_{\text{EtOH}}\) (H\(_2\) yield rate = 205 μmol g-cat\(^{-1}\) s\(^{-1}\)). Similar poor performance was also observed on 1%Rh/\(\text{La}_2\text{O}_2\text{CO}_3\) (Rh/L, \(x = 1\)), XRD result confirmed the support existed as \(\text{La}_2\text{O}_3\) usually occurred at temperatures above 873 K \([9]\). Clearly, the OSR reaction was greatly enhanced by La doping into \(\text{CeO}_2\), particularly when La reached 30 mol. % \((x = 0.3)\), at which point the catalyst exhibited the best performance for ethanol conversion and the highest H\(_2\) yield. On Rh/\(\text{CL}_0.3\), 100% ethanol conversion was achieved at 573 K with H\(_2\) yield of 214 μmol g-cat\(^{-1}\) s\(^{-1}\), which was 4.2 times more than that of Rh/C. Note that the ethanol conversion and H\(_2\) yield of Rh/\(\text{CL}_0.3\) at 573 K is higher than that of Rh/C at 723 K. Over the whole tested temperature region (473–723 K), the H\(_2\) yield order of the catalysts series was Rh/\(\text{CL}_0.3\) > Rh/\(\text{CL}_0.4\) > Rh/\(\text{CL}_0.5\) > Rh/\(\text{CL}_0.2\) > Rh/\(\text{CL}_0.1\) > Rh/L.

To further reveal the significant promotion due to La doping, the distributions of carbonaceous compounds (denoted as \(S_x\)) over the Rh/C and Rh/\(\text{CL}_0.3\) catalysts are shown in Fig. 2, in which the total height corresponds to the ethanol conversion (mass balances 100 ± 3%). CH\(_3\)CHO, which has been regarded as a main precursor for coke deposits \([20]\), was undetected in our case over both of the catalysts. This means that the ceria-based supported catalysts favor ethanol dehydrogenation to CH\(_3\)CHO rather than dehydration to CH\(_2\)CH\(_2\), which was also reported by Zhang et al. \([36]\). The acid-base properties of the metal oxides were measured by NH\(_3\)-TPD method \((\text{Fig. S1, see also Supplementary Material})\). The low NH\(_3\) desorption indicates a lack of acidic sites in Ce–La solid solution, favoring dehydrogenation reaction, while disfavoring ethanol dehydration to CH\(_2\)CH\(_2\) and thus guaranteeing a long duartiality of Rh/\(\text{CL}_0.3\).
Compared with Rh/C, introduction of La further accelerates the dehydrogenation reaction, resulting in a high concentration of CH$_3$CHO and thus a high H$_2$ yield on the La-doped catalyst. At 473 K, the concentration of CH$_3$CHO over Rh/CL0.3 was up to 41%, which is about twice of that of Rh/C. When the temperature increased to 523 K, the concentration of CH$_3$CHO clearly decreased, particularly on Rh/CL0.3, which was accompanied by the formation of CO$_2$, CO and CH$_4$ and a higher H$_2$ yield. Further increasing the temperature to 573 K resulted in a disappearance of CH$_3$CHO, at which point the ethanol conversion reached 100% for Rh/CL0.3. At the same temperature, however, the ethanol conversion on Rh/C was less than 50% and CH$_3$COCH$_3$ began to be generated. After La doping, CH$_3$COCH$_3$ was undetected within the investigated temperature range. As we expected, Rh/CL0.3 sharply decreased the CO selectivity, giving the lowest CO concentration of below 350 ppm in the total gas flow (selectivity < 0.5%) at 673 K. This result possibly indicates that a WGS reaction was initiated by La doping [31] or as WGS reaction generally takes place simultaneously with many other reactions during OSR, and La doping may promote its contribution. In addition, CH$_4$, which competes for H atoms with H$_2$, is a serious issue for reforming running for H$_2$ production at low temperature, the occurrence of which was pronounced over Rh/CL0.3 at temperatures above 523 K, needed to be further improved.

More importantly, the stability study presented in Fig. 3 indicates that the addition of La to Rh/C catalyst can greatly enhance its life span. Over Rh/CL0.3, stable ethanol conversion, high H$_2$ yield and low CO selectivity (<1.4%) were maintained during 60 h of on-stream operation at 673 K. In contrast, a sharp deactivation was observed for the Rh/C catalyst after 12 h reaction, during which the H$_2$ yield was reduced from 1.3 to 0.4 mol/mol$_{\text{EtOH}}$. At the beginning of the stability test, it should be noted that about 10% CH$_3$COCH$_3$ was produced over the Rh/C catalyst, while this value decreased to 2.3% after the 12 h test, and then below the limit of detection after 24 h. When considering that after the 24 h aging test there were no more noticeable changes in ethanol conversion and H$_2$ yield over the Rh/C catalysts, the formation of CH$_3$COCH$_3$ and its further transformation to coke is inferred to
account for the deactivation of the catalyst during the OSR reaction. The following intermediate reaction study (Fig. 5) confirmed that Rh/Cl0.3 exhibited excellent stability for ethanol reforming due to the high CH₃COCH₃ conversion activity.

### 3.2. Intermediate reactions

The above results confirmed that both the pure and La-doped ceria-supported Rh catalysts (Rh/C and Rh/Cl0.3) favored ethanol dehydrogenation to CH₃CHO (Eq. (6)) rather than dehydration to CH₂CH₂ (Eq. (7)). La doping greatly promoted the formation of CH₃CHO at the low temperature of 473 K (Fig. 2) which was totally converted at a raised reaction temperature (>753 K). It is a great enhancement compared to Rh/C. To clarify the effect of La doping for CH₃CHO production and its conversion, 10% CH₃CHO (CH₃CHO: EtOH = 10%) was introduced into the feed gas of the OSR reaction, then the distributions of products were measured over the Rh/Cl0.3 and Rh/C catalysts, respectively. Based on these results, the yield changes (d_X) of X during the OSR reaction over the two catalysts were calculated and are shown in Fig. 4.

**Ethanol dehydrogenation to CH₃CHO:**

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \tag{6}
\]

**Ethanol dehydration to CH₂CH₂:**

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O} \tag{7}
\]

Even though 10% CH₃CHO was introduced into the feed gas, this species was hardly observed after being exposed to Rh/Cl0.3 within the temperature range of 573–723 K, indicating a high efficiency for the transformation of CH₃CHO. During this process, CH₃COCH₃ was also below the detectable limit, giving d(CH₃CHO) = d(CH₃COCH₃) = 0 and therefore not shown in Fig. 4. The reaction pathway can be described as follows (detail explanation can be found in Supplementary Material):

- **CH₃CHO decomposition reaction [19,36]:**
  \[
  \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} \tag{8}
  \]
- **CH₄ steam reforming reaction:**
  \[
  \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \tag{9}
  \]
- **CO gas water shift reaction:**
  \[
  \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \tag{10}
  \]
Over the Rh/C catalyst, introduction of 10% CH₂CHO results in an increase of its concentration in the reforming process, giving $d_{CH₂CHO}$ of 7.2% at the temperature of 573 K, indicating that this catalyst is not as active as Rh/CL0.3 for the transformation of CH₂CHO. Meanwhile, the presence of CH₂CHO with high concentration inhibits the conversion of ethanol and formation of final products, giving a $d_{CH₂COCH₃}$ of 3%, and thus negative yields for H₂, CO₂, and CH₄. With temperature increasing, increases in H₂, CO₂, and CH₄ yields were clearly observed with a decrease in the value of $d_{CH₂CHO}$, which, in turn, indicates the reaction pathway of CH₃CHO over the Rh/C catalyst. As shown in Fig. 4B, introduction of CH₃CHO also results in the formation of CH₃COCH₃, particularly at low temperatures. As reported by Zhang et al., CH₃COCH₃ was formed via decarbonylation of CH₃CHO (Eq. (11)) over ceria-supported Ir catalyst [36]. However, in our case, the highest increase of CH₃CHO yield was less than 1.5% after 10% CH₃CHO addition, which means that the main pathway of CH₃COCH₃ formation possibly follows another reaction. For example, CH₃CHO formation via aldol condensation, followed by dehydrogenation (Eq. (12)), has also been reported [4]. Besides, the limited increase of $d_{CH₂COCH₃}$ may also had some relationship with reaction conditions.

\[
2\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2 \quad (11)
\]

\[
2\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + 4\text{H}_2 \quad (12)
\]

The stability tests showed that the Rh/C catalyst with higher selectivity for CH₃COCH₃ was much more unstable than Rh/CL0.3. And aldol condensation of CH₃COCH₃ followed by dehydration to mesityl oxide (Eq. (13)) was reported to be one of the main coke formation reactions leading to catalyst deactivation [4]. Therefore, to clarify the enhancement of stability after La doping, the CH₃COCH₃ conversion reaction over Rh/C and Rh/CL0.3 catalysts needs to be further studied.

\[
2\text{CH}_3\text{COCH}_3 \rightarrow (\text{CH}_3)_2\text{C(OH)}\text{CH}_2\text{COCH}_3 
= (\text{CH}_3)_2\text{C} = \text{CHCOCH}_3 \quad (13)
\]

Fig. 5 shows the changes of product yields over Rh/CL0.3 and Rh/C catalysts after 10% CH₃COCH₃ (CH₃COCH₃: EtOH = 10%) was added to the feed gas of the OSR reaction. Over the Rh/CL0.3 catalyst, ethanol, CH₃CHO and CH₃COCH₃ remained undetected no matter whether CH₃COCH₃ was added or not, so their changes are not shown in Fig. 5A. This means that the added CH₃COCH₃ can easily totally convert over the Rh/CL0.3 catalyst. The change of $d_{CH₃COCH₃}$ within ±0.2% over the whole time range means that CH₃COCH₃ was totally converted to H₂, CO₂, and CH₄ at 673 K, giving the values of $d_{H₂} = 21\%$, $d_{CO₂} = 24\%$, and $d_{CH₄} = 6\%$, respectively. Therefore, CH₃COCH₃ is proposed to convert following the two reactions below and detail explanation can be found in Supplementary Material.

\[
\text{CH}_3\text{COCH}_3 + \text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2 \quad (14)
\]

\[
\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{CH}_4 \quad (15)
\]

Eq. (15) can be considered as the combination of Eqs. (14) and (16). This means that the CO WGS reaction plays an important role in the CH₃COCH₃ removal reaction.

\[
\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightarrow \text{CO} + 2\text{CH}_4 \quad (16)
\]

CO + H₂O $\rightarrow$ CO₂ + H₂ (10)

Over the Rh/C catalyst, addition of CH₃COCH₃ into the feed gas caused quite different results in ethanol reforming compared with that of Rh/CL0.3. Large amounts of CH₃COCH₃ were still present in the outlet gas (the right axis), which resulted in a significant decrease in ethanol conversion, and thus the yields of H₂, CO₂, CH₄, and CO, particularly in the initial 2 h. The deactivation induced by CH₃COCH₃ introduction, within 6 h in this case, was worse than that occurring in the 60 h aging test that was shown in Fig. 3. Indeed, the used catalyst turned totally black, which further confirmed that the production of a high concentration of CH₃COCH₃ was the main reason for coke deposition and deactivation of the Rh/C catalyst at 673 K in the OSR reaction.

As described above, the water gas shift reaction also contributed to the OSR of ethanol. To clarify its role, 1% CO and 3% water were fed through Rh/CL0.3 and Rh/C catalysts under the same space velocity with the OSR reaction. As shown in Fig. 6, over the Rh/CL0.3 catalyst, the CO conversion is detectable even at a temperature as low as 473 K. In the temperature range of 598–763 K, CO was undetectable (the detection limit of CO is above 200 ppm). However, for the Rh/C catalyst, the CO conversion increases slowly with increasing temperature, reaching 100% conversion at a temperature as high as 723 K. Comparing these two catalysts, it is not difficult to deduce that good water gas shift activity helps a great deal in lowering CO selectivity in the OSR reaction.

### 3.3. Characterization of catalysts

The BET surface area and porosity values of Rh/CLx catalysts are shown in Table 1. The surface area of the samples increased from 44 m² g⁻¹ (Rh/C) to 147 m² g⁻¹ (Rh/CL0.2) with La doping, but with further increases in La content, the surface area decreased to 125, 73 and 40 m² g⁻¹ for Rh/CL0.3, Rh/CL0.5, and Rh/CL0.7, respectively. The BET surface area and CO coverage of Rh/CLx catalysts after 10% CH₃COCH₃ (CH₃COCH₃: EtOH = 10%) are shown in Fig. 2A. The surface area decreased from 44 m² g⁻¹ (Rh/C) to 35 m² g⁻¹ (Rh/CL0.3) with La doping.

![Fig. 6](image)

**Fig. 6** – The concentration of CO over Rh/CL0.3 (●) and Rh/C (∗) catalysts and concentration of H₂ over Rh/CL0.3 (●) and Rh/C (●) catalysts for WGS reaction from 473 K to 723 K. Reaction conditions: catalysts weight 100 mg (40–60 mesh), H₂O = 3%, CO = 1%, total flow rate = 350 mL min⁻¹ (N₂ balance).
CL0.4 and Rh/CL0.5, respectively. Introduction of La significantly changed the surface area of the prepared samples, however, the trend of surface area versus La/Ce ratio did not follow that of the H₂ yield over the corresponding catalysts presented in Fig. 1, indicating that this property is not directly responsible for H₂ production from ethanol reforming over the different catalysts.

The XRD patterns of the fresh Rh/CLx catalysts are shown in Fig. 7. Rh/C exhibited the characteristic diffractogram of the cubic fluorite structure of CeO₂ (JCPDS 34-0394). XRD analysis also revealed that Rh/L could be assigned to the typical La₂O₂CO₃ structure (JCPDS 37-0804), while for the other samples, no peaks due to La compounds were observed. Considering that the ionic radius of La³⁺ (0.11 nm) is larger than that of Ce⁴⁺ (0.097 nm), substituting La³⁺ into the CeO₂ lattice should result in expansion of the CeO₂ lattice [29]. With La doping, the cell parameter a (Table 1) gradually increased from 5.40 Å (Rh/C) to 5.52 Å (Rh/CL0.5) (the XRD results were refined by Rietveld analysis), indicating the formation of a Ce₁₋ₓLaₓOₙ solid solution. The shift of the CeO₂ characteristic peaks to lower angles, and the intensity of the peaks decreasing with La³⁺ loading also confirmed the tuning of the fluorite cubic structure of CeO₂ [37,38]. The XRD results of used Rh/C and Rh/CL0.3 catalysts were showed in Table S1 (Supplementary Material), exhibiting very tiny changes of particle size and cell parameter “a”.

In the Raman spectroscopy (Fig. 8) characterizations, a strong band at ~460 cm⁻¹ corresponding to the F₂g mode of fluorite CeO₂ was observed for all of the cerium-containing samples. As ceria is doped with La³⁺, the F₂g mode becomes asymmetric and shifts slightly to lower wavenumbers with a decreasing intensity. This is the result of combined effects: deformation taking place in the crystal structure due to the larger ionic radius of La³⁺ compared to Ce⁴⁺, lattice expansion and the presence of oxygen vacancies [29]. The band at ~1077 cm⁻¹ has always been accepted as the A₁g mode of La₂O₂CO₃, and it was not observed in La-doped ceria. This result indicates that a Ce—La solid solution was formed, which is consistent with the XRD results. The band at about 600 cm⁻¹ was associated with oxygen vacancies, which are generated to maintain the electrostatic balance of Ce³⁺/La³⁺-containing fluorite ceria. The intensity of the band due to oxygen vacancies gradually increased with increasing La content, indicating that higher La content gives a higher density of oxygen vacancies. Further evidence for the formation of oxygen vacancies in the Rh/Clx catalysts was identified in the Ce 3d and O 1s XPS analysis (Table 2).

The objective of the X-ray photoelectron spectra (XPS) analysis was to investigate the valence states of the components of the Rh/Clx samples. Fig. S2 shows the Ce 3d XPS spectra of the Rh/Clx catalysts, together with the corresponding peak-fitting results listed in Table S2 (see supplementary information). The Ce³⁺/(Ce³⁺ + Ce⁴⁺) and (Ce³⁺ + La³⁺)/(Ce + La) were calculated by analysis of the integrated peak areas of Ce³⁺ and Ce⁴⁺, and the results are shown in Table 2. Note that the (Ce³⁺ + La³⁺)/(Ce + La) in Rh/CL0.4 and Rh/CL0.5, respectively. Introduction of La significantly changed the surface area of the prepared samples, however, the trend of surface area versus La/Ce ratio did not follow that of the H₂ yield over the corresponding catalysts presented in Fig. 1, indicating that this property is not directly responsible for H₂ production from ethanol reforming over the different catalysts.

Table 1 — Physical properties of Rh/CLx catalysts that measured by BET and XRD.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area/m² g⁻¹</th>
<th>Pore volume/cc g⁻¹</th>
<th>Average pore diameter/nm</th>
<th>Cell parameter a/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/C</td>
<td>44</td>
<td>2.7</td>
<td>3.2</td>
<td>5.40</td>
</tr>
<tr>
<td>Rh/CL0.1</td>
<td>57</td>
<td>3.9</td>
<td>2.9</td>
<td>5.43</td>
</tr>
<tr>
<td>Rh/CL0.2</td>
<td>147</td>
<td>7.5</td>
<td>1.6</td>
<td>5.46</td>
</tr>
<tr>
<td>Rh/CL0.3</td>
<td>125</td>
<td>7.0</td>
<td>1.8</td>
<td>5.49</td>
</tr>
<tr>
<td>Rh/CL0.4</td>
<td>73</td>
<td>5.6</td>
<td>2.4</td>
<td>5.50</td>
</tr>
<tr>
<td>Rh/CL0.5</td>
<td>40</td>
<td>2.5</td>
<td>3.5</td>
<td>5.52</td>
</tr>
<tr>
<td>Rh/L</td>
<td>13</td>
<td>1.3</td>
<td>8.0</td>
<td>–</td>
</tr>
</tbody>
</table>

a The cell parameter a was calculated through XRD data after Rietveld analysis.
CLx catalysts increase with La doping, thus also increasing the oxygen vacancies that are created due to the substitution of Ce\(^{4+}\) cations with La\(^{3+}\)/Ce\(^{3+}\) cations [29].

The XPS Rh 3d spectra show a doublet centered at around 309 and 314 eV. These peaks correspond to the binding energy of Rh 3d5/2 and Rh 3d3/2, respectively, with a spin-orbit coupling of about 5 eV, which is close to the value for Rh\(^{3+}\) in the Rh/CLx catalysts (Fig. 9) [25]. Over all the samples, no Rh entities were observed in TEM images, indicating a high dispersion of Rh (Fig. S3). Under the reaction conditions, however, the produced H\(_2\) or the reaction intermediates are expected to reduce RhO\(_x\) species, resulting in changes in the catalyst structure and then the reactivity. Therefore, the sample of Rh/CL0.3 was pretreated by 30% H\(_2\) at 723 K for 1 h, and then its activity for OSR reaction was measured, with the result shown in Fig. S4. Compared with the fresh sample, reduction pretreatment induces slight decreases in ethanol conversion and H\(_2\) yield at temperatures below 623 K, while hardly changes the catalytic property at temperatures higher than 623 K. This result indicates that reduction of RhO\(_x\) only decreases in some degree the activity of catalyst for ethanol reforming at low temperatures, which was further confirmed by the second run (Fig. S4) and the long-term activity test (Fig. 3, operating at 673 K).

The O 1s core level spectra of the Rh/CLx catalysts are presented in Fig. 10. The peak with low binding energy (529–530 eV) is attributed to the lattice oxygen ions (O\(^2^-\)) of the crystalline network [29]. On the high binding energy side at 531.5–532 eV (\(\Delta E_B \approx 2.4\) eV), different assignments are made according to different objects [39,40]. However, it has been acknowledged that the high binding energy peak corresponds to oxygen species located on the surface and more easily reduced by H\(_2\). Therefore, we call this species “surface oxygen” (OS), and calculated its percentage contribution to total oxygen (O\(_T\) = O\(^2^-\) + O\(_S\)), as summarized in Table 2 along with lattice oxygen.

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![Fig. 9 – XPS Rh 3d spectra of Rh/CLx catalysts.](image)

![Fig. 10 – XPS O 1s spectra of Rh/CLx catalysts.](image)
This result suggests that the properties of oxygen in the catalysts may play a crucial role in the ethanol reforming process, which needs further confirmation.

To highlight the reducibility of Rh/CLx during the OSR reaction, in our case, H2 temperature-programmed reduction (H2-TPR) was performed on Rh/CLx catalysts (Fig. 11A), during which two typical peak reduction profiles were observed (except for Rh/L), located at 440–460 K and 585–605 K, respectively. The low-temperature peak is related to the reduction of surface oxygen species [40] and Rh3+ in Rh2O3, combined with the reduction of surface CeO2 at the interface with Rh2O3 (denoted as reducible surface species, thereafter) [41], which was confirmed by quantifying the H2 consumption. Take Rh/CL0.3 as an example, the amount of hydrogen consumed at low temperatures was 0.523 mmol g⁻¹, which was much higher than that required for complete reduction of Rh2O3 to Rh (0.146 mmol g⁻¹, in theory) (Fig. S5). The reduction of the bulk oxygen of La2O2CO3 occurred above 800 K (result not shown here). It should be noted that an increased reducibility of surface species and bulk oxygen was created by La doping, which can further tuned by optimizing the ratio of Ce/La.

The ethanol conversion and H2 production was observed even at a temperature as low as 473 K, at which point the reduction of bulk oxygen did not occur, while there is a close relationship between the reducibility of surface species and the performance of Rh/CL in the OSR reaction. The larger the amount of H2 consumption related to reducible surface species (Fig. 11), the higher the ethanol conversion and H2 production (Fig. 1), which possibly suggests that the reducibility of surface species on Rh/CL catalysts plays a key role in ethanol reforming at temperatures below 573 K. At temperatures above 573 K, the reduction of lattice oxygen was triggered, which may further facilitate ethanol conversion (Fig. 1). Among these catalysts, the sample of Rh/CL0.3 possesses the most plentiful reducible surface species, whose reduction was shown to occur at the lowest temperatures. At the same time, this catalyst also gives the largest amount of reducible lattice oxygen. Coincidentally, Rh/CL0.3 has the best ethanol conversion and H2 yield. If one integrates the areas of H2 consumption peaks for Rh/CLx in the low and high temperature ranges (Fig. 11B), it is not difficult to find that the relative amount of H2 consumption is in the order Rh/CL0.3 > Rh/CL0.4 > Rh/CL0.5 > Rh/CL0.2 > Rh/CL0.1 > Rh/C ≈ Rh/L, exhibiting exactly the same tendency as the H2 yield and ethanol conversion (Fig. 1). This result possibly indicates that the OSR performance of Rh/CLx catalysts has a very close relationship with their reducibility.

Generally, the total H2 consumption revealed by the H2-TPR characterization is not close to what can be expected to be realized in actual operation at a given temperature. As a result, the OSC, which also indicates the redox property of Rh/CLx catalysts, was measured by the TG method to explain the high degree of enhancement due to La doping [42]. In this analysis, the sample was purged in Ar and then reduced in 5.2% H2 (Ar-balance) and oxidized in 10% O2 (Ar-balance) repeatedly at 673 K. Fig. 12 compares the weight change of the Rh/C and Rh/CL0.3 catalysts exposed to H2/Ar and O2/Ar alternately. The stable weight loss and gain during this cyclic experiment indicates that the reduction and oxidization of
these catalysts are reversible. The average weight change of Rh/C was 0.21%, giving an OSC of 131 μmol-O g-catalyst⁻¹, while the change of Rh/CL0.3 was up to 0.41%, corresponding to a high OSC of 256 μmol-O g-catalyst⁻¹. As expected, meanwhile, the high OSC of Rh/CL0.3 guarantees its long durability for the OSR reaction by suppressing the formation of CH₃COCH₃ (Fig. 3) and its further transformation to H₂ and CO₂ (Fig. 5).

The Rh dispersion on Ce–La solid solution is also an important issue for OSR reaction, which was measured by chemical adsorption method at 223 K. After using 2 h at 673 K under OSR reaction, the Rh dispersions of Rh/C and Rh/CL0.3 were 63% and 93%, respectively. This result suggests that La doping promotes the dispersion of Rh, which also contributes to the high performance of Rh/CL0.3 for ethanol reforming. For the Rh/C and Rh/CL0.3 catalysts, no matter fresh or used samples, no species of Rh can be found in TEM images (Fig. S3, Supplementary Material), which further confirms the high dispersion of Rh.

4. Discussion

Based on the detailed analysis of the final products obtained during OSR and the intermediate reaction test, a reaction scheme for ethanol reforming taking place on Ce–La solid-solution-supported Rh catalysts can be drawn, as shown in the following illustration (Scheme 1).

The initial reaction is ethanol dehydrogenation to CH₃CHO rather than dehydration to CH₂CH₂. With increasing temperature, CH₃CHO totally decomposed to CH₄ and CO. CH₂COCH₃ can be produced from CH₃CHO decarboxylation or directly converted from ethanol, then rapidly reacts with O₂ to CO₂ and H₂ or decomposes to CO and CH₄. Because of the high CO WGS and CH₄ steam reforming activity of the catalyst, CO and CH₄ will further convert to CO₂ and H₂, which are the ideal products of ethanol oxidative steam reforming.

The XRD and Raman results confirmed the formation of Ce–La solid solution after La doping into ceria. Compared with pure ceria-supported Rh (Rh/C), the Ce–La solid-solution supported Rh catalysts exhibit higher surface areas, higher density of oxygen vacancies and better reducibilities. However, for this catalyst series (Rh/CLₓ), the highest surface area (Rh/CL0.2) cannot guarantee the best catalytic activity, which is different from the inert SiO₂-supported Ni catalysts for hydrogen production from ethanol [43].

Defects such as oxygen vacancies dominate the electronic and chemical properties of ceria and ceria-based catalysts, leading to their important roles in catalytic applications such as automotive exhaust catalysis and WGS reactions [11,24]. It is widely accepted that oxygen vacancies present in great numbers on the ceria and La–Ce solid solution [44,45]. As for ethanol reforming, oxygen vacancies that presented at the metal-CeO₂ interface had been regarded as the active sites for the formation of surface oxygen and –OH groups [46,47]. These oxygen vacancies at the metal-CeO₂ interface were also responsible for the adsorption of ethanol and its further transformation to surface ethoxy species, as a key intermediate for ethanol reforming. On such oxygen vacancies, the proximity of ethoxy species to active oxygen species (surface oxygen and/or –OH groups) thus promoted surface reaction pathways of ethanol reforming, which have been described above. Differently, according to Noronha et al. [4] and Ozkan’s [10] work, C₂H₅OH may converts to ethoxy/acetate species on the support, and then transfer to the metal-support interface for C–C scission. Considering oxygen vacancies enriched at the metal-support interface, their roles in ethanol reforming also can not be ignored.

The increased density of oxygen vacancies induced by La doping indicates that the introduction of low-valent cations into the CeO₂ lattice can further tune its properties, which was indicated by our Raman characterization and XPS analysis, and is in agreement with the results of Reddy et al. [29]. As revealed by H₂-TPR measurement, this defective structure promotes oxygen mobility and thus reduction of Rh/CLₓ compared with that of Rh/C. Meanwhile, an interesting point which needs to be addressed here is that the high density of oxygen vacancies created by La doping does not always provide good reducible performance for Rh/CLₓ. As suggested by Trovarelli, the oxygen vacancies created by introduction of aliovalent ions such as La³⁺ and Gd³⁺ into CeO₂ can be regarded as extrinsic vacancies, an increase of which does not provide higher reducibility unless oxygen mobility or the uptake rate is sufficiently fast [44]. With this in mind, it is easy to understand why only the oxygen vacancies at the metal-CeO₂ interface have been regarded as the active sites for the surface reactions of ethanol reforming [46–48]. This result also indicates that the Ce/La ratio should be optimized to obtain Rh/CL with better reducibility and the Rh/CL0.3 catalyst with the highest reducibility may correspond to the most abundant active sites for ethanol conversion.

The increased reducibility of surface species created by La doping is beneficial for ethanol dehydrogenation to CH₃CHO at low temperatures, prompting ethanol conversion and H₂ production (Figs. 1 and 2, and Scheme 1). This increase in reducibility infers higher surface oxygen mobility that benefits the oxidation of CH₃CHO to acetate species, which may further decompose to the final products of H₂, CO₂ and CH₄ (Fig. 4) at low temperatures. It is in agreement with the findings of Noronha and co-workers [46–48]. Over the La-doped catalyst, the higher mobility of surface oxygen also enhanced the CO WGS reaction, further increasing H₂ yield while decreasing the concentration of CO (Figs. 2 and 6, and Scheme 1). The relationship between the reducibility of the Rh/CLₓ catalyst and the La content is in good agreement with that of ethanol conversion and H₂ yield on the corresponding catalyst, revealing the key role of reducible species in the OSR reaction [49]. Still, the detailed mechanism on how the reducible species participate in the ethanol reforming remains unclear, the understanding of which will be the focus of our next research study.

\[\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4\]

\[\text{CH}_2\text{COCH}_3 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\]

\[\text{CH}_2\text{COCH}_3 + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2\]

\[\text{CH}_2\text{COCH}_3 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\]

\[\text{CH}_3\text{CHO} + \text{H}_2\rightarrow \text{CH}_4 + \text{CO}\]

\[\text{Scheme 1} - \text{The OSR reaction network over Ce–La solid solution supported Rh catalyst.}\]
It is widely accepted that the migration of oxygen in ceria and ceria-based materials takes place via a vacancy-hopping mechanism [45,50]. In the presence of oxygen, the higher density of oxygen vacancies induced by La doping and high oxygen mobility indicates a higher OSC property of Rh/CL0.3 compared with that of Rh/C, which has been confirmed by our TG measurement. Such enhancement results in a high efficiency of Rh/CL0.3 for CH3COCH3 transformation to the final products of CO2, CH4, and H2, identified by the CH3COCH3 addition experiment (Fig. 5), also in agreement with the proposal of Noronha and co-workers [46–48]. Over Rh/CL, meanwhile, the consumption of active oxygen species by CH3COCH3 transformation can be immediately replenished by oxygen in the gas phase, keeping the reaction operating efficiently, and thus a long durability for the OSR reaction can be expected and realized successfully.

It has been found that Ce–La supported Au catalyst has better WGS reaction activity than pure ceria-supported catalyst due to the greater number of oxygen vacancies introduced by La3+ [31,32]. Herein, we confirmed that the enhancement of redox properties by La doping is also a benefit for the WGS reaction at low temperatures over the ceria-supported Rh catalyst (Fig. 6), resulting in a lower CO selectivity during the OSR reaction over the Rh/CL0.3 catalyst (Figs. 2 and 3).

5. Conclusions

A series of Ce–La solid solutions have been prepared by a simple urea co-precipitation method. Optimized La doping clearly promotes the accessibility of surface-reducible species on ceria-supported Rh catalysts, particularly at low temperatures. This promotion is of benefit for the formation of acetaldehyde and its further transformation into final products. The close relationship between the reducibility of La3+-doped ceria-supported Rh catalysts and their performance in ethanol reforming has revealed the decisive role of OSC in the ethanol conversion and H2 yield. An enhanced redox property of Rh/CL also contributes to a decrease in the concentrations of CH3COCH3 and CO, and thus a long durability for H2 production can be expected and realized successfully. This finding may provide a new guideline for understanding the mechanism of the OSR reaction and for the creation of catalysts with very high performance for H2 production.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.ijhydene.2013.05.137.

References


