available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Celebrating the 70th Anniversary of Dalian Institute of Chemical Physics, CAS)

Activation of small molecules over praseodymium-doped ceria

Meiling Guo ^a, Xuebin Liu ^a, Angelo Amorelli ^{b,*}^a Energy Innovation Laboratory, BP (China) Dalian Office, Dalian 116023, Liaoning, China^b Group Research, BP International, Sunbury, TW16 7LN, United Kingdom

ARTICLE INFO

Article history:

Received 29 January 2019

Accepted 4 April 2019

Published 5 November 2019

Keywords:

CeO₂

Pr dopant

Oxygen vacancy

Degree of reduction

Propane dehydrogenation

ABSTRACT

Praseodymium can modify the properties of ceria (CeO₂), changing the electronic structure, reducibility and catalytic behavior. Oxygen vacancies in the ceria-based samples can activate C–O and C–H bonds of small molecules such as CO₂ and propane. Partially reduced Pr/CeO_{2-x} can selectively activate C–H of propane, giving a propylene selectivity of ca. 75% at a propane conversion of 5% to 10%. Excess reduction of Pr/CeO_{2-x} induces coking reactions during propane dehydrogenation, resulting in fast catalyst deactivation.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Al₂O₃ and ZrO₂ are widely applied as catalyst supports and binders in petrochemical industries. Non-reducible Al₂O₃ is often regarded as an inert support or binder, but the high temperature treatment of Al₂O₃ can generate activity for the non-oxidative dehydrogenation of isobutane to isobutylene [1]. The active sites on Al₂O₃ are attributed to the lattice defects created by removal of surface hydroxyl groups during high temperature treatment [1]. Bulk ZrO₂-based materials with lattice defects have been identified as active catalysts for propane dehydrogenation [2]. The activity of ZrO₂ can be improved by metal doping (such as La₂O₃-doped ZrO₂) to increase the reducibility of ZrO₂ and oxygen vacancies [3]. It is proposed that zirconium cations located near oxygen vacancies are catalytically active sites for the propane dehydrogenation [2,3]. It is desirable to know if the oxygen vacancies on reducible ceria-based materials could be active for the activation of C–H and C–C bonds of light alkanes like non-reducible Al₂O₃ and

ZrO₂ abovementioned.

CeO₂ is a reducible oxide that is widely applied as a support or promoter in catalytic materials because of its unique redox properties [4–10]. When used as a support, CeO₂ is able to trap Pt atoms in an ionic form, enhancing the Pt dispersion and inhibiting Pt sintering in catalysts for the non-oxidative propane dehydrogenation [11,12]. As a promoter (< 1 wt%), CeO₂ can tune the propane dehydrogenation performance and improve the stability of PtSn/Al₂O₃ [13]. In many cases, CeO₂ in combination with noble metals leads to superior catalytic performance. Knowledge on the role of CeO₂ itself (without loading conventional hydrogenation/dehydrogenation metals) in C–H and C–C bond activation of light alkanes is still limited.

Doping with metals of lower valence states is an effective way to induce the formation of oxygen vacancies in CeO₂. Extensive studies have focused on 3d transition metal (Ni²⁺, Co²⁺, Cr³⁺, etc.)-doped CeO₂ [14–16]. However, it is suggested that transition metal ions do not incorporate into the oxide lattices but instead phase segregate into transition metal oxide nano-

* Corresponding author. E-mail: angelo.amorelli@bp.com

DOI: S1872-2067(19)63369-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 11, November 2019

particles [17]. Such problems could be overcome in rare earth metal-doped CeO₂, in which the rare earth ions can achieve full dissolution into the CeO₂ lattice. Among the various rare earth elements used as dopants for ceria catalysts, praseodymium has received a significant interest over the last few years [18–21]. Pr species embedded into the ceria lattice promote the formation of oxygen vacancies and the mobility of negatively charged ions in the solid framework [18]. Moreover, our recent studies have shown that the oxygen vacancies induced by the Pr doping of CeO₂ promotes the catalytic performance of the Prins condensation-hydrolysis of isobutene with formalin [22,23].

The aim of this work is to investigate the structures of defects, the reducibility of Pr-doped CeO₂, and its capability for the activation of small molecules (CO₂ and propane) in the absence of hydrogenation/dehydrogenation metals (e.g. Pt or CrO_x etc.). Pr/CeO₂ was prepared by a co-precipitation method and characterized by X-ray diffraction (XRD), UV-Vis absorption spectrophotometry, and Raman spectrometry. The reducibility of Pr/CeO₂ was investigated by temperature-programmed reduction (TPR) in hydrogen. The degree of reduction was further characterized by titration using CO₂ as a probe molecule by the temperature-programmed surface reaction (CO₂-TPSR). CO₂ reduction with hydrogen (H₂ & CO₂-TPSR) was used as a probe reaction to investigate the influence of the degree of reduction on the catalytic performance. Finally, propane dehydrogenation was used as a model reaction to evaluate C–H and C–C activation by the oxygen vacancies. This work will help understand the inherent catalytic properties of ceria-based materials and explore the potential of oxygen vacancies in metal oxide catalysts for light hydrocarbon conversion.

2. Experimental

2.1. Catalyst preparation

Pr-doped CeO₂ catalyst with a Ce/Pr molar ratio of 4:1 was prepared by a co-precipitation method [22]. 4 g of Ce(NO₃)₃·6H₂O and 1 g of Pr(NO₃)₃·6H₂O were dissolved in 100 mL of deionized water. The ammonium hydroxide solution was added drop-wise to the solution whilst stirring to maintain a pH of 11 and the solution was subsequently stirred for 2 h. The mixture was filtered and dried at 120 °C for 12 h, and the recovered solid calcined at 550 °C under a flow of air (50 mL min^{−1}) for 4 h to obtain the final material. For comparison a CeO₂ sample was also prepared without adding the Pr dopant.

2.2. Catalyst characterization

XRD patterns were collected on a PANalytical X'Pert powder diffractometer using Cu K_α radiation, operated at 40 kV and 40 mA. UV-Vis absorption spectra were recorded on a JASCO V650 UV-Vis spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried out on a Netzsch TG-DTA apparatus (Netzsch, Germany). About 10 mg sample was placed in an Al₂O₃ crucible and heated at a ramping rate of 10 °C min^{−1} under an air flow of 20 mL min^{−1}.

Visible Raman spectra were collected on the Renishaw micro-Raman spectrometer equipped with a CCD detector using the laser wavelengths of 785 and 532 nm. UV Raman spectra were collected using a home-built spectrometer with a laser wavelength of 325 nm (Kimmon Co). All spectra were calibrated by placing the main Raman peak of monocrystalline Si at 520 cm^{−1}. For most experiments, the laser power at the sample was kept below 1 mW to prevent burning effects.

For *operando* UV Raman experiments, a 30 mg catalyst sample was loaded in an in-situ cell and purged with helium at 400 °C for 30 min. Subsequently the feed gas (2 vol% H₂) was introduced with a flow rate of 25 mL min^{−1} at 400 °C and then ramped to the desired temperature under the flow of hydrogen. The catalyst sample was characterized on-line with the UV Raman spectrometer while the effluent was on-line analyzed using a Pfeiffer quadrupole mass spectrometer to monitor the profile of hydrogen and water as a function of time and temperature.

H₂-TPR experiments were performed with a Quantachrome autosorb iQ. First, 50 mg sample was loaded in a U-shaped quartz reactor and purged with helium to remove the adsorbed species at 500 °C for 30 min with a heating rate of 10 °C min^{−1}. After cooling to 40 °C, the purge gas was switched to a feed of 3 vol% H₂ in helium with a flow rate of 30 mL min^{−1}. The H₂-TPR experiment was carried out with a heating rate of 10 °C min^{−1} up to the desired temperature. The effluent was monitored with a thermal conductivity detector (TCD) and a Pfeiffer quadrupole mass spectrometer. The amount of hydrogen consumed per catalyst mass was calculated according to the TCD signals. The integrated area translated to the amount of hydrogen consumption using calibrated curves of the hydrogen amount to the peak area.

The procedure for TPSR was similar to the H₂-TPR but used the feeds described in Table 1. The following mass to charge (*m/z*) signals were monitored: 44 (CO₂), 40 (Ar), 32 (O₂), 28 (CO), 18 (water), 4 (He), 2 (H₂).

2.3. Propane dehydrogenation test

Propane dehydrogenation tests were carried out in a tubular quartz reactor with an inner diameter of 10 mm at 570 °C and atmospheric pressure. 200 mg of catalyst (40–60 mesh) was diluted with 250 mg of quartz sand. Prior to catalytic performance tests, the as-synthesized samples were pretreated with Ar at 550 °C for 1 h or 5 vol% H₂/Ar at 550 (650) °C for 1 h, corresponding to the propane performance testing over Pr/CeO₂ or the pre-reduced Pr/CeO_{2-x} at 550 (650) °C, respectively. Then propane feed (4 vol% propane, 2 vol% N₂ in He)

Table 1
Feeds for the TPSR.

Experiment	Feed diluted in helium or argon
H ₂ -TPR	3 vol% H ₂
CO ₂ -TPSR	2 vol% CO ₂
H ₂ & CO ₂ -TPSR	2 vol% CO ₂ and 2 vol% H ₂
TPO (temperature-programmed oxidation)	3 vol% O ₂

was introduced through the catalyst bed at a total flow rate of 40 mL min⁻¹. The effluent was analyzed on-line using an Agilent MicroGC 490. Nitrogen was used as an internal standard for the performance calculations. Hydrogen, nitrogen, methane, and CO were analyzed with a molecular sieve column and TCD. CO₂, ethylene, and ethane were analyzed using a PoraPLOT U column and TCD. Propane and propylene were analyzed with an aluminum oxide column and TCD. The partial pressures of the unconverted feed and products were directly determined using calibrated micro-GC. The flow rates of the unconverted feed and collected products were calculated based on the internal standard, nitrogen. The conversion of propane was determined as the amount of reacted propane divided by the amount of propane at the reactor inlet. The carbon selectivity of each compound was calculated as the quantity of the product formed divided by the amount of converted propane. The fitted hydrogen was calculated according to the below two equations:

Partial pressure of fitted H₂ = 4/3 × Partial pressure of CO + Partial pressure of propylene

3. Results and discussion

3.1. Characterizations (XRD, UV-Vis Absorption spectroscopy, and Raman spectroscopy)

Fig. 1a shows the XRD patterns of as-synthesized CeO₂ and Pr/CeO₂. The observed peaks in the XRD patterns are well indexed and consistent with the reference data of CeO₂, which indicates the single phase cubic fluorite structure. The optical properties of CeO₂ and Pr/CeO₂ were characterized by UV-Vis absorption spectroscopy shown in Fig. 1b. The spectrum of CeO₂ shows a strong absorption band below 400 nm, which originates from the O²⁻ to Ce^{3+/4+} charge transfer transition [24]. Pr/CeO₂ shows a high intensity visible light absorption in 400–650 nm, which has been assigned to the charge transfer transition from O²⁻ to Pr^{3+/4+} [24–27].

Raman spectroscopy is a useful technique in the characterization of defects of the oxide samples. The defects of CeO₂ were studied by Raman spectroscopy using 785, 532, and 325 nm

excitation laser lines (Fig. 2a). The spectra excited with the 785 and 532 nm laser lines both have a single band at 460 cm⁻¹. The spectrum excited with the 325 nm laser line shows a band at 460 cm⁻¹ and another band centered at 590 cm⁻¹. The band at 590 cm⁻¹ can be explained by a resonance Raman effect, since CeO₂ strongly absorbs in the UV region around 325 nm as shown in Fig. 1b [28].

The bands at 460 and 590 cm⁻¹ are related to the Raman-active vibrational mode (F_{2g}) of fluorite-type structure and the defects of CeO₂, respectively [27,29]. The F_{2g} band is the symmetrical stretching vibration of the oxygen atoms around cerium ions. The defect species characterized by the band at 590 cm⁻¹ was observed under ambient conditions and its concentration may be low as it cannot be observed without the resonance enhancement effect.

To validate the structure of the defect characterized by the band at 590 cm⁻¹, CeO₂ was studied by *operando* UV Raman spectroscopy (Fig. 2b). Compared to the spectrum obtained under ambient condition shown in Fig. 2a, there are no changes of the band at 590 cm⁻¹ after helium and hydrogen treatments at 400 °C. This band shifts to 570 cm⁻¹ upon the hydrogen treatment at elevated temperature such as 550 and 650 °C shown in Fig. 2b. The shift of band occurs upon on-line hydrogen treatment and should be related to the oxygen vacancy produced by the hydrogen treatment [30]. The consumption of the hydrogen and formation of water were observed by an on-line mass spectrometer during the *operando* Raman test in Fig. S1, confirming the formation of oxygen vacancies induced by the hydrogen reduction of CeO₂.

The Pr/CeO₂ shows the different optical properties with strong absorbance in the visible region as shown in Fig. 1b. The impact of the Pr dopant on the structure and amount of the defects was investigated by Raman spectroscopy as shown in Fig. 3a. The spectrum of Pr/CeO₂ excited with 785 nm laser line shows a vibrational band of fluorite-type structure at 455 cm⁻¹ and a weak peak centered at 570 cm⁻¹. The spectrum collected with 532 nm excitation laser line is different to the spectrum collected with 785 nm excitation laser line. The peak area ratios of the bands at 570 and 455 cm⁻¹ are 0.2 and 3.3 for the spectra collected with the excitation laser lines of 785 and 532 nm, respectively. This difference can be explained by a resonance

Fig. 1. XRD patterns (a) and UV-Vis absorption spectra (b) of CeO₂ and Pr/CeO₂.

Fig. 2. Raman spectra of CeO₂ excited with 785, 532, and 325 nm laser lines (a) and *operando* UV Raman spectra of CeO₂ (b).

Fig. 3. Raman spectra of Pr/CeO₂ excited with 785, 532, and 325 nm laser lines (a) and *operando* UV Raman spectra of Pr/CeO₂ (b).

Raman effect, since Pr/CeO₂ strongly absorbs in the visible region around 532 nm as marked in Fig 1b. Compared with the visible Raman results, the 325 nm excited UV Raman shows a band centered at 590 cm⁻¹ rather than 570 cm⁻¹ and the peak area ratio of the bands at 590 and 460 cm⁻¹ is further increased to 6.7.

For Pr/CeO₂, the band around 570–590 cm⁻¹ might be related to the intrinsic defects of CeO₂ (590 cm⁻¹), the Pr³⁺ induced oxygen vacancy (570 cm⁻¹) and the vibration of the Pr–O species around 550 cm⁻¹ [31]. Due to complexities of the band and the resonance Raman effect (resulting in different peak area ratios between the band at 570–590 and 455 cm⁻¹ for different laser lines), the amount of the defects cannot be directly calculated by Raman results. However, the shift of the band of fluorite-type structure from 460 to 455 cm⁻¹ confirms that the Pr dopant changes the local structure of the sample as shown in Fig. S2.

To validate the structure and the evolution of defects in Pr/CeO₂, an *operando* UV Raman test was performed and the results are shown in Fig. 3b. The band at 590 cm⁻¹ shifts to 570 cm⁻¹ upon hydrogen treatment at elevated temperature such as 550 and 650 °C. Combined with the on-line mass spectrometer results, this suggests that the Raman band shift is related to the

formation of oxygen vacancies induced by hydrogen treatment. This band shift is similar to the above CeO₂ test results shown in Fig. 2b.

3.2. Temperature programmed reactions (H₂-TPR, CO₂-TPSR, and H₂ & CO₂-TPSR)

The reducibility of CeO₂ and Pr/CeO₂ was investigated by temperature-programmed reactions. The H₂-TPR profiles of the CeO₂ and Pr/CeO₂ samples are shown in Fig. 4a and 4b, respectively, and the characteristic data derived from these profiles are listed in Table 2. For CeO₂, two reduction zones were observed. The low-temperature region (350–630 °C) corresponds to surface reduction while the high-temperature region (>630 °C) is assigned to bulk reduction in agreement with previous publications [8,32]. The hydrogen consumption of CeO₂ drops to zero at 630 °C, suggesting that this temperature is the boundary temperature for the surface and bulk reduction under the testing condition. The surface reduction of CeO₂ can be well deconvoluted into the peaks of α and β with the peak area ratio of 1:1. The surface and overall hydrogen consumptions of CeO₂ are 0.28 and 0.38 mmol g⁻¹, respectively. The overall hydrogen consumption amount is similar to the previously re-

Fig. 4. H₂-TPR TCD signals of CeO₂ (a) and Pr/CeO₂ (b).

Table 2

H₂-TPR quantitative analysis results for CeO₂ and Pr/CeO₂.

Sample	H ₂ consumption (mmol g ⁻¹)				<i>x</i> after reduction (Pr) CeO _{2-x}
	Surface (350–630 °C)			Bulk (630–800 °C)	
	Peak α	Peak β	Peak γ		
CeO ₂	0.14	0.14	—	0.10	0.065
Pr/CeO ₂	0.27	0.1	0.13	0.19	0.118

ported result of 0.34 mmol g⁻¹ [33].

The respective surface and overall hydrogen consumptions of Pr/CeO₂ are 0.5 and 0.69 mmol g⁻¹ as listed in Table 2. The Pr dopant not only increases the amount of hydrogen consumption but also tunes the material's reduction characteristics: (i) the peak area ratio of α and β increases from 1 to 2.7; (ii) a new type of surface reduction peak γ is formed; (iii) surface and bulk oxygen reduction cannot be distinguished clearly. The Pr-doped material still consumes hydrogen at 630 °C, which is different to the CeO₂.

H₂-TPR was also monitored using a mass spectrometer, allowing the observation of hydrogen consumption and water formation. For Pr/CeO₂ in Fig. 5a, the hydrogen starts decreasing

as the temperature reaches ca. 350 °C while the water signal is observed at the same time. Maxima in the amount of hydrogen consumed are centered at 480 and 570 °C, coinciding with maxima in the amount of water produced. The mass spectra confirm that Pr/CeO₂ is reduced by H₂ producing water. After H₂ reduction, Pr/CeO₂ is in its reduced state, i.e. Pr/CeO_{2-x}, where *x* indicates the amount of oxygen vacancies and its value is listed in Table 2.

CO₂ was used as a probe molecule to titrate the degree of reduction generated by the hydrogen treatment as a function of temperature. Before CO₂-TPSR, the as-synthesized Pr/CeO₂ was pre-reduced in a flow of hydrogen at 450, 550, 650 or 700 °C for 30 min. Then CO₂-TPSR was carried out in a flow of CO₂

Fig. 5. H₂-TPR profiles of Pr/CeO₂ (mass spectrometer signal) (a) and CO₂-TPSR over the pre-reduced Pr/CeO_{2-x} as a function of pre-reduction temperature (b).

from 300 to 600 °C with a heating rate of 10 °C min⁻¹. As shown in Fig. 5b, over the Pr/CeO_{2-x} pre-reduced at 700 °C, the CO₂ signal starts decreasing as the temperature reaches 400 °C and CO production is observed at the same time. This result suggests that CO₂ can dissociate on oxygen vacancies releasing CO, while the catalyst reverts from a reduced state to the initial oxidized state. The amount of CO relates to the degree of reduction and is lower with lower hydrogen pre-reduction temperatures. It is interesting to note that the pre-reduced sample at 450 °C shows little activity for the CO₂ reduction.

CO₂ reduction with hydrogen (H₂ & CO₂-TPSR) was used as a probe reaction to validate the influence of the degree of reduction on the reaction performance. As shown in Fig. 6a, the initial surface reduction of Pr/CeO₂ in a H₂ & CO₂-TPSR experiment is quite similar to that observed in the H₂-TPR experiment (Fig. 4b). Both show a starting reduction temperature around 350 °C and a peak of hydrogen consumption around 480 °C. In addition, there is no CO₂ consumption and CO formation below 480 °C. This indicates that oxygen vacancies are generated at an early stage, corresponding to a low degree of reduction, and do not interact with CO₂ at all. This result is similar to that observed in the CO₂-TPSR experiment for the material pre-reduced at 450 °C in Fig. 5c. It is interesting to observe that CO₂ consumption occurs between 480 and 520 °C but without CO generation. It seems that oxygen vacancies are generated in this stage, corresponding to low-level degree of reduction, interact with CO₂ but are unable to decompose CO₂ into CO. Further consumption of both H₂ and CO₂ was observed above 520 °C along with the formation of water and CO. Obviously, oxygen vacancies generated at this stage, corresponding to a higher degree of reduction of Pr/CeO₂, can convert CO₂ into CO.

The CO₂ reduction to CO shown in Fig. 6a happens at 520 °C, much higher than the 400 °C in the CO₂-TPSR over pre-reduced Pr/CeO_{2-x} (Fig. 5c). To address this, a H₂ & CO₂-TPSR experiment was performed over the hydrogen pre-reduced Pr/CeO_{2-x} and the result is shown in Fig. 6b. As expected, CO₂ was converted to CO over Pr/CeO_{2-x} starting at 400 °C instead of 520 °C, indicating that the activity of oxygen vacancies generated relates to the material's degree of reduction. As shown in Fig. 6c and Fig. S3, the profiles of CeO₂ are similar to that of Pr/CeO₂, and the difference is the lower amount of water in the region of

350–520 °C, in agreement with the H₂-TPR results in Fig. 4.

As discussed above, H₂ & CO₂-TPSR results suggest that the ceria catalyst is reduced by H₂ generating oxygen vacancies. Subsequently CO₂ can be dissociated on the oxygen vacancies releasing CO, while the catalyst changes back from the reduced state to the initial oxidized state. The catalyst cycle between the oxidized and reduced state initiates the CO₂ reduction with hydrogen so that the overall reaction is reverse water gas shift.

3.3. Catalytic performance (propane dehydrogenation)

Propane activation reaction was used as a model reaction to investigate the influence of the degree of reduction and Pr dopant on the catalytic performance. This reaction was explored at a constant temperature of 570 °C. The performance results of Pr/CeO₂ are summarized in Fig. 7 and Table 3. The sum of products carbon selectivities is the carbon molar ratio between the collected products and converted propane and its decrease indicates an obvious carbon loss in the later stage of the reaction, which should be in the form of coking. TGA and TPO analysis of the used catalyst confirms a carbon deposit about 3 wt% of the catalyst weight in Fig. S4. The reaction process can be divided into a relative stable stage and a fast coking stage. As shown in Fig. 7 and Table 3, the stable stage exhibits the following trends: (i) the initial activity is low and the activity gradually increases with time on stream (TOS); (ii) propylene is the main product and its selectivity increases quickly with time and then stabilizes at ca. 75%; (iii) CO selectivity increases first and then stabilizes at ca. 15%; (iv) CO₂ is only detected at the initial time on stream. The formation of CO and CO₂ implies that Pr/CeO₂ is reduced by propane in the early stage of the reaction. The material's degree of reduction keeps increasing, corresponding to more oxygen vacancies on the catalyst. The oxygen vacancies seem selective for the activation of the C–H rather than C–C bonds of propane, giving much higher propylene and lower ethylene yields. The product distribution suggests that the major reactions over Pr/CeO₂ are catalyst reduction and dehydrogenation of propane presented by the following equations:

The hydrogen partial pressure was fitted based on the CO

Fig. 6. H₂ & CO₂ co-feed experiments for Pr/CeO₂ (a), 600 °C hydrogen pre-reduced Pr/CeO_{2-x} (b), and CeO₂ (c).

Fig. 7. Conversion and the sum of selectivities (a), main product selectivity (b), and collected hydrogen and fitted hydrogen (c) as a function of time on stream for Pr/CeO₂.

and propylene partial pressure using the two equations above. The collected hydrogen and fitted hydrogen are in good agreement for the relative stable performance stage shown in Fig. 7c.

The fast coking stage exhibits the following trends: (i) the conversion of propane does not start to drop until significant carbon deposits have built up; (ii) side reaction $C_3H_8 \rightarrow 3C$ (coke) + $4H_2$ occurs in the coking stage, which is confirmed by the carbon loss along with the big difference between the collected and fitted hydrogen partial pressure, which indicates the boundary of relative stable stage and fast coking stage; (iii) propylene selectivity is still around 50%.

The degree of reduction and activity of the oxygen vacancies of Pr/CeO₂ can be tuned by the hydrogen reduction temperature as shown in Fig. 5b. The sample pre-reduced by hydrogen at 650 °C has higher degree of reduction than the sample pre-reduction by hydrogen at 550 °C. The performance data of the Pr/CeO_{2-x} formed by pre-reduction in hydrogen at 550 and 650 °C are given in Fig. 8 with the reference of Pr/CeO₂. The Pr/CeO_{2-x} produced by pre-reduced in hydrogen at 650 °C exhibits higher initial activity and propylene selectivity. This result is in agreement with the activity observed in the CO₂ reduction experiments (Fig. 5b) and further confirms that the oxygen vacancies have the ability to activate the C–H bonds of propane producing propylene as shown in Fig. 8a and 8b. The CO₂ formation by full oxidation of propane is greatly or fully eliminated for Pr/CeO_{2-x} formed by pre-reduction by hydrogen at 550 and 650 °C as shown in Fig. 8c. The CO formation is also

obviously lower for the hydrogen pre-reduced samples as shown in Fig. 8d.

The performance of propane conversion over CeO₂ is summarized in Fig. S5 and Table S1. The performance profiles over CeO₂ are similar to that of Pr/CeO₂, but the selectivities for partial oxidation product CO, selective dehydrogenation product propylene, and the coke formation are different, as shown in Fig. 9. The typical performance data of CeO₂ and Pr/CeO₂ are compared at similar propane conversions (Fig. 9a), aiming to investigate the impact of the Pr dopant on the product selectivities. For the relatively stable performance stage (entries 1–5), Pr/CeO₂ gives higher selectivity to propylene, lower selectivity to CO, and lower selectivity to coke as shown in Fig. 9b, 9c and 9d, respectively. For the fast coking stage (entries 6–8), the product selectivities of the two samples are similar, exhibiting much higher coke selectivity around 27%–31% due to the side reaction of $C_3H_8 \rightarrow 3C$ (coke) + $4H_2$.

Based on the above results, the oxygen vacancies seem responsible for the selective activation of the C–H bonds of propane resulting in propylene formation. During the early stable performance stage the activity is proportional to the amount of oxygen vacancies. Increases in the amount of oxygen vacancies (high degree of reduction) induce side reactions like the decomposition of propane to coke (carbon deposits) and hydrogen. The carbon deposition causes the deactivation of the catalyst. The Pr dopant suppresses the formation of byproducts of CO and coke in the initial stable stage, giving higher propylene

Table 3

The typical propane activation reaction performance data for Pr/CeO₂.

Entry No	TOS (h)	Conversion (%)	Product carbon selectivity (C mol%)						Carbon balance	
			Propylene	Ethylene	Ethane *	Methane	CO	CO ₂ *	Sum	(%)
1	0.82	5.0	75.0	3.2	0	6.5	15.7	0.4	100.8	100.0
2	0.93	6.0	74.4	2.6	0	6.8	15.1	0.2	99.1	99.9
3	1.04	7.3	75.0	2.0	0	7.3	15.6	0.1	100.0	100.0
4	1.10	8.3	74.2	1.8	0	7.7	15.7	0.1	99.5	100.0
5	1.15	9.6	73.8	1.5	0	8.1	16.6	0.1	100.1	100.0
6	1.82	9.1	62.1	1.2	1.3	2.4	4.6	0	71.6	97.4
7	1.88	7.8	61.7	1.5	1.5	2.5	4.2	0	71.4	97.8
8	1.96	6.2	58.9	1.9	1.9	2.8	3.8	0	69.3	98.1

*Concentrations of the ethane (entries 1–6) and CO₂ (entry 6–9) were below the GC limit of detection.

Fig. 8. Conversion (a), propylene selectivity (b), CO₂ selectivity (c), and CO selectivity (d) as a function of time on stream for Pr/CeO_{2-x} formed by the hydrogen pre-reduction at 550 and 650 °C with comparison to the results for Pr/CeO₂.

Fig. 9. Conversion (a), propylene selectivity (b), CO selectivity (c), and coke selectivity (d) for CeO₂ and Pr/CeO₂. Coke selectivity is estimated from the carbon loss calculated by the sum of products detected by GC. The negative coke selectivity is due to the precision of the GC quantification (1% error bar).

selectivity. The propane conversion over a non-metal loaded Pr/CeO₂ catalyst is very appealing with a 75% selectivity to propylene at a propane conversion around 5%–10%. More work is under way to understand and stabilize the oxygen vacancies over Pr/CeO₂.

4. Conclusions

In this study, the defects of CeO₂ and Pr/CeO₂ are investigated by Raman spectroscopy with different excitation laser lines and an *operando* UV Raman technique, providing infor-

mation of the structure and amount of defects, and their evolution at elevated temperatures under the flows of He and H₂. The reducibility of Pr/CeO₂ is investigated by the reactions of hydrogen. The oxygen vacancies of the reduced PrCeO_{2-x} have the ability to activate the C–O bond of CO₂ (CO as the product) and C–H bonds of propane (propylene as the product). The activity and product selectivity relate to its degree of reduction. Pr dopant not only changes the optical properties, the amount and type of defects, and reducibility characteristics, but also changes the selectivities of the propane activation reaction suppressing the formation of byproducts CO and coke and producing higher propylene selectivity. The degree of reduction of the ceria sample is an important descriptor of the catalytic performance.

Acknowledgments

We acknowledge Dr. Zhixin Zhang at Dalian Institute of Chemical Physics with the support of catalyst preparation. We thank Benjamin Dennis-Smith and Glenn Sunley from BP International for fruitful discussions.

References

- [1] U. Rodemerck, E. V. Kondratenko, T. Otroshchenko, D. Linke, *Chem. Commun.*, **2016**, 52, 12222–12225.
- [2] T. Otroshchenko, J. Radnik, M. Schneider, U. Rodemerck, D. Linke, E. V. Kondratenko, *Chem Commun.*, **2016**, 52, 8164–8167.
- [3] T. Otroshchenko, S. Sokolov, M. Stoyanova, V. A. Kondratenko, U. Rodemerck, D. Linke, E. V. Kondratenko, *Angew. Chem. Int. Ed.*, **2015**, 54, 15880–15883.
- [4] L. Vivier, D. Duprez, *ChemSusChem*, **2010**, 3, 654–678.
- [5] J. Ke, J.-W. Xiao, W. Zhu, H. Liu, R. Si, Y.-W. Zhang, C.-H. Yan, *J. Am. Chem. Soc.*, **2013**, 135, 15191–15200.
- [6] S. Chen, L. Luo, Z. Jiang, W. Huang, *ACS Catal.*, **2015**, 5, 1653–1662.
- [7] N. L. Wieder, M. Cargnello, K. Bakmutsky, T. Montini, P. Fornasiero, R. J. Gorte, *J. Phys. Chem. C*, **2011**, 115, 915–919.
- [8] K. Ahn, D. S. Yoo, D.H. Prasad, H.-W. Lee, Y.-C. Chung, J.-H. Lee, *Chem. Mater.*, **2012**, 24, 4261–4267.
- [9] X. Zhang, Y. Song, F. Guan, Y. Zhou, H. Lv, G. Wang, X. Bao, *J. Catal.*, **2018**, 359, 8–16.
- [10] Q. Xie, H. Zhang, J. Kang, J. Cheng, Q. Zhang, Y. Wang, *ACS Catal.*, **2018**, 8, 4902–4916.
- [11] H. Xiong, S. Lin, J. Goetze, P. Pletcher, H. Guo, L. Kovarik, K. Artyushkova, B. M. Weckhuysen, A. K. Datye, *Angew. Chem. Int. Ed.*, **2017**, 56, 8986–8991.
- [12] Y. Nagai, T. Hirabayashi, K. Dohmae, N. Takagi, T. Minami, H. Shinjoh, S. I. Matsumoto, *J. Catal.*, **2006**, 242, 103–109.
- [13] S. Zhou, Y. Zhou, J. Shi, Y. Zhang, X. Sheng, Z. Zhang, *J. Mater. Sci.*, **2015**, 50, 3984–3993.
- [14] A. Thurber, K. M. Reddy, V. Shutthanandan, M. H. Engelhard, C. Wang, J. Hays, A. Punnoose, *Phys. Rev. B*, **2007**, 76, 165206.
- [15] B. Vodungbo, Y. Zheng, F. Vidal, D. Demaille, V. H. Etgens, D. H. Mosca, *Appl. Phys. Lett.*, **2007**, 90, 062510.
- [16] N. S. Ferreira, L. G. Abraçado, M. A. Macêdo, *Phys. B*, **2012**, 407, 3218–3221.
- [17] G. Niu, E. Hildebrandt, M. A. Schubert, F. Boscherini, M. H. Zoellner, L. Alff, D. Walczyk, P. Zaumseil, I. Costina, H. Wilkens, T. Schroeder, *ACS Appl. Mater. Interfaces*, **2014**, 6, 17496–17505.
- [18] T. Andana, M. Piumetti, S. Bensaid, N. Russo, D. Fino, R. Pirone, *Appl. Catal. B*, **2016**, 197, 125–137.
- [19] T. Andana, M. Piumetti, S. Bensaid, N. Russo, D. Fino, R. Pirone, *Nanoscale Res. Lett.*, **2016**, 11, 278.
- [20] E. Poggio-Fraccari, B. Irigoyen, G. Baronetti, F. Mariño, *Appl. Catal. A*, **2014**, 485, 123–132.
- [21] A. Davó-Quinonero, J. González-Mira, D. Lozano-Castelló, A. Bueno-López, *Catal. Lett.*, **2018**, 148, 258–266.
- [22] Z. Zhang, Y. Wang, J. Lu, J. Zhang, M. Li, X. Liu, F. Wang, *ACS Catal.*, **2018**, 8, 2635–2644.
- [23] Z. Zhang, Y. Wang, J. Lu, C. Zhang, M. Wang, M. Li, X. Liu, F. Wang, *ACS Catal.*, **2016**, 6, 8248–8254.
- [24] L. Li, F. Chen, J.-Q. Lu, M.-F. Luo, *J. Phys. Chem. A*, **2011**, 115, 7972–7977.
- [25] I. Tankov, K. Arishtirova, J. M. C. Bueno, S. Damyanova, *Appl. Catal. A*, **2014**, 474, 135–148.
- [26] B. Matovic, S. Boskovic, M. Logar, M. Radovic, Z. Dohcevic-Mitrovic,

Graphical Abstract

Chin. J. Catal., 2019, 40: 1800–1809 doi: S1872-2067(19)63369-3

Activation of small molecules over praseodymium-doped ceria

Meiling Guo, Xuebin Liu, Angelo Amorelli *

BP (China) Dalian Office, China; BP International, United Kingdom

The praseodymium-doped ceria material in the absence of hydrogenation/dehydrogenation metals can selectively activate C–H bond of propane, giving a propylene selectivity of ca. 75% at a propane conversion of 5% to 10%.

- Z. V. Popovic, F. Aldinger, *J. Alloys Compd.*, **2010**, 505, 235–238.
- [27] M. Guo, J. Lu, Y. Wu, Y. Wang, M. Luo, *Langmuir*, **2011**, 27, 3872–3877.
- [28] F. Fan, Q. Xu, H. Xia, K. Sun, Z. Feng, C. Li, *Chin. J. Catal.*, **2009**, 30, 717–739.
- [29] S. Bensaid, M. Piumetti, C. Novara, F. Giorgis, A. Chiodoni, N. Russo, D. Fino, *Nanoscale Res. Lett.*, **2016**, 11, 494.
- [30] Z. Wu, M. Li, J. Howe, H. M. Meyer, S. H. Overbury, *Langmuir*, **2010**, 26, 16595–16606.
- [31] V. K. Tripathi, R. Nagarajan, *Solid State Sci.*, **2018**, 84, 1–7.
- [32] S. M. Schimming, G. S. Foo, O. D. LaMont, A. K. Rogers, M. M. Yung, A. D. D'Amico, C. Sievers, *J. Catal.*, **2015**, 329, 335–347.
- [33] S. Pradhan, D. C. Upham, H. Metiu, E. W. McFarland, *Catal. Sci. Technol.*, **2016**, 6, 5483–5493.

镨掺杂氧化铈材料在小分子活化中的应用

郭美玲^a, 刘雪斌^a, Amorelli Angelo^{b,*}

^a碧辟能源创新实验室, 碧辟(中国)大连办公室, 辽宁大连 116023, 中国

^b英国石油公司, 森伯里, 英国

摘要: 氧化铈材料具有独特的氧化还原特性, 常作为优异载体或助剂广泛应用于多种催化反应. 未负载常规活性金属的氧化铈作为助剂在低碳烷烃的活化研究中非常有限. 我们前期研究发现, 镨掺杂的氧化铈(Pr/CeO_2)可高效催化异丁烯与甲醛水溶液的Prins缩合-水解反应. 本文在此基础上研究了 Pr/CeO_2 材料对 CO_2 和丙烷等小分子的活化, 并将反应活性及选择性与材料的还原度(氧空位浓度)相关联. 结果表明, 与未掺杂的氧化铈材料相比, Pr/CeO_2 可显著提高材料的表面还原度. 通过进一步调变氢气预还原温度得到了一系列具有不同还原度的材料, 它们展示出对 CO_2 (C–O键)不同的活化性能. 不同还原度的 Pr/CeO_2 催化丙烷脱氢的反应活性及产物的选择性与其还原度有关, 氧空位是丙烷脱氢的活性中心, 可选择性地活化丙烷中的C–H键. Pr/CeO_2 材料在5%–10%丙烷转化率条件下可获得75%的丙烯选择性.

关键词: 氧化铈; 镨掺杂; 氧空位; 还原度; 丙烷脱氢

收稿日期: 2019-01-29. 接受日期: 2019-04-04. 出版日期: 2019-11-05.

*通讯联系人. 电子信箱: angelo.amorelli@bp.com

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).