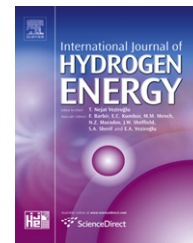




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Syn-gas generation in the absence of oxygen and isotopic exchange reactions over Rh & Pt/doped-ceria catalysts

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ARTICLE INFO

Article history:

Received 9 August 2011

Received in revised form

25 October 2011

Accepted 30 October 2011

Available online 25 November 2011

Keywords:

Syn-gas

Methane decomposition

Oxygen isotopic exchange

Doped ceria

Hydrogen

ABSTRACT

Syn-gas generation in the absence of oxygen by methane decomposition offers an interesting route to decrease reactor size and cost because methane is the only reactant in the gas phase. In this work, several catalysts were studied, Rh/CeO₂, Pt/CeO₂, Rh/(Ce_{0.91}Gd_{0.09})O_{2-x}, Pt/(Ce_{0.91}Gd_{0.09})O_{2-x}, Rh/γ-Al₂O₃ and Pt/γ-Al₂O₃ for methane reforming in the absence of gaseous oxygen. Rhodium showed a superior catalytic activity and selectivity with respect to Pt. This catalytic behavior may be due to the strong metal-support interaction, associated with the formation of mixed metal-oxide species at the interface. The addition of Gd³⁺ to ceria lowered the required temperatures for catalyst activation with respect to the un-doped material. Conversely to oxygen ion conducting materials, which showed a high selectivity for syn-gas generation, the non-oxygen conducting catalysts did not generate carbon monoxide. These results may be correlated to their oxygen storage capacity and ionic conductivity. Since gaseous oxygen was not delivered to the reactor, it is clear that the only source of oxygen was the catalyst. During the isothermal isotopic oxygen exchange experiments over Pt/(Ce_{0.91}Gd_{0.09})O_{2-x} and Pt/γ-Al₂O₃, results illustrated that oxygen in the gas phase was exchanged with the oxygen from the catalyst. Three different molecules were detected ¹⁶O–¹⁸O, ¹⁶O–¹⁶O and ¹⁸O¹⁸O. A higher amount of oxygen was exchanged over Pt/(Ce_{0.91}Gd_{0.09})O_{2-x} with respect to Pt/γ-Al₂O₃. It is proposed that mainly lattice and surface oxygen were exchanged over Pt/(Ce_{0.91}Gd_{0.09})O_{2-x} and Pt/γ-Al₂O₃, respectively. It is also suggested that two types of reaction mechanisms take place, the simple and multiple hetero-exchange with the participation of one and two catalyst oxygen atoms, respectively. Similarly to methane reforming, lower temperatures were required for the oxygen exchange experiments over Rh than over Pt, as illustrated by results of the temperature-programmed exchange reactions. In summary, the properties of doped ceria may open new catalytic routes for oxidation reactions without gaseous oxygen because post-oxidation can restore its oxygen storage capacity.

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1. Introduction

In the literature, methane decomposition is seen as an interesting route for the CO₂-free hydrogen production. The catalytic decomposition of methane could be a promising pro-

ecological method for hydrogen production. The main drawback of this process is fast deactivation of the catalyst by the carbonaceous deposit formed on its surface. The catalyst can be regenerated by oxidation processes and re-used in the catalytic reactions. Applications of these carbon deposits have

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been suggested, as fuel for direct carbon fuel cells, as catalyst and catalyst supports. Their addition into polymers could result in high quality composites. Since they are electrically conductive with good thermal conductivity and mechanical strength, they have a great potential for additional utilization purposes [1]. Catalysts containing Ni and Fe have been widely tested for methane decomposition. However, Ni-based catalysts are limited because they are not stable above 600 °C, which restrain the production of highly concentrated Hydrogen streams. In the other hand, Fe-based catalysts show stability at higher temperatures, up to 1000 °C. Unfortunately, these catalysts have a shorter lifetime due to deactivation during repeated cycles [2]. Thus, although Ni and Fe have some advantages, noble metals may still be preferred due to lower tendency for coking. Most literature reporting methane decomposition show Hydrogen and carbon deposits as the only products, few references report syn-gas generation. Ceria has been previously studied for methane decomposition and found that besides Hydrogen, CO is also generated from the reaction between the carbon deposits and the lattice oxygen. An enhancement in Hydrogen production was observed over Fe–CeO₂ with respect to Fe₂O₃, which was explained by the spillover of carbonyls and reverse spillover of oxygen [3].

The direct utilization of ceria-based materials for oxidation reactions are attractive because they are able to promote catalytic processes in the absence of oxygen. The re-oxidation of these materials can restore their oxygen storage capacity (OSC). Ceria has been investigated as a major component of three-way catalysts in automobile applications because of the oxygen storage and release capacity, which allows controlling the oxygen stoichiometry in the exhaust. The non-stoichiometric CeO_{2-x} (0 ≤ x ≤ 0.28) enables to restore oxygen deficiency under oxidation conditions to form stoichiometric CeO₂, a process that is accompanied by reversible transformation between two oxidation states, Ce⁴⁺ and Ce³⁺. Because of this property, oxides whose composition is in the range Ce₂O₃–CeO₂ can be formed. In the literature, thermodynamic data indicate that cerium metal is unstable in the presence of oxygen. The final stoichiometry is strongly dependent on temperature and oxygen pressure. Reduced ceria results from the removal of oxygen ions from ceria lattice, which generates anion vacancies. It has been proposed that these oxygen vacancy defects are reactive sites on the surface of metal oxides containing ceria. The extremely open structure of the fluorite assembly tolerates a high level of atomic disorder, which may be introduced either by reduction or by doping. When an aliovalent solute is dissolved in CeO₂, the crystal lattice must compensate for the excess negative charge. Dopant addition to ceria has shown to enhance ionic conductivity and oxygen storage capacity. Ionic conductivity of ceria is a function of content and type of dopant and results from minimum activation energy and/or maximum solubility of the two oxides. Ceria-based oxides have been studied in various reactions, for example, hydrocarbon oxidation, water–gas shift, steam reforming, etc. The attractive possibility of using CO₂ as an oxidizing agent opens a route to technically important reactions such as syn-gas production in the absence of oxygen [4–13].

The combination of noble metals and doped-ceria in catalytic materials for the partial oxidation of methane to

generate syn-gas in the presence of gaseous oxygen has been successfully demonstrated. The properties of doped ceria such as oxygen storage capacity and ionic conductivity may allow utilizing these materials for a new process, syn-gas production from methane reforming in the absence of oxygen. Synthesis gas can be directly delivered to SOFCs or utilized in the Fischer–Tropsch process to produce liquid hydrocarbons, just to mention few applications. The catalysts can be regenerated in another reactor by oxidation reactions. Here, results are reported on the production of syn-gas by methane decomposition having methane as the only reactant in the gas phase, utilizing materials that have previously shown successful results in the presence of gaseous oxygen [14–19].

The objective of this work was to study the catalytic properties of Pt and Rh supported on ceria doped oxides for methane reforming in the absence of gaseous oxygen. Isotopic exchange reactions between oxygen in the gas phase and oxygen in the catalyst were also studied. Catalysts supported on γ -alumina were also tested, for comparison purposes.

2. Experimental

2.1. Syn-gas generation in the absence of gaseous oxygen

Rh/CeO₂, Pt/CeO₂, Rh/(Ce_{0.91}Gd_{0.09})O_{2-x} (Rh/GDC10), Pt/(Ce_{0.91}Gd_{0.09})O_{2-x} (Pt/GDC10) and Rh/ γ -Al₂O₃ were studied during the catalytic partial oxidation of methane in the absence of gaseous oxygen. A sample of 100 mg was loaded into the chamber of a flow catalytic reactor. Experimental tests were conducted with CH₄ (5 Vol. %)/He at a flow rate of 25 ml/min. To start the experiments, the reactor was pre-heated at 100 °C. Then, the temperature was increased to 700 °C at 10 °C/min. A mass spectrometer was connected online to the catalytic reactor to analyze the feed and product gas streams. A cold trap at the outlet of the reactor condensed any water out of this stream. Catalyst synthesis methods and characterization have been published somewhere else [14–17].

2.2. Isothermal isotopic oxygen exchange reactions

The first step during the isothermal isotopic oxygen exchange (IIOE) reactions was to test the quartz reactor for any catalytic activity. Following, the catalyst was reduced under a Hydrogen atmosphere from 40 to 700 °C at a heating rate of 15 °C/min. Hydrogen was flushed from the reactor with Helium before increasing the temperature to 850 °C, then, the reactor was cooled down to 700 °C. At this temperature, the catalysts were dosed with ¹⁸O₂ (Speciality Gases, 20 Vol. %)/He pulses into a continuous 50 ml/min He stream. These tests were performed in a flow reactor with an inner diameter of 1.2 cm. The reactor exit was connected through a heated inlet capillary system to a mass spectrometer to monitor the exit gas composition. These experiments had two objectives, to study IIOE reactions and to label the catalysts with ¹⁸O₂. Further temperature-programmed isotopic exchange (TPIE) experiments were conducted over ¹⁸O labeled catalysts. These tests were performed as a function of temperature in a ¹⁶O₂

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