Hydrogen Production from a Combination of the Water–Gas Shift and Redox Cycle Process of Methane Partial Oxidation via Lattice Oxygen over LaFeO₃ Perovskite Catalyst

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Received: August 23, 2006; In Final Form: October 12, 2006

A redox cycle process, in which CH₄ and air are periodically brought into contact with a solid oxide packed in a fixed-bed reactor, combined with the water–gas shift (WGS) reaction, is proposed for hydrogen production. The sole oxidant for partial oxidation of methane (POM) is found to be lattice oxygen instead of gaseous oxygen. A perovskite-type LaFeO₃ oxide was prepared by a sol–gel method and employed as an oxygen storage material in this process. The results indicate that, under appropriate reaction conditions, methane can be oxidized to CO and H₂ by the lattice oxygen of LaFeO₃ perovskite oxide with a selectivity higher than 95% and the consumed lattice oxygen can be replenished in a reoxidation procedure by a redox operation. It is suggested that the POM to H₂/CO by using the lattice oxygen of the oxygen storage materials instead of gaseous oxygen should be possibly applicable. The LaFeO₃ perovskite oxide maintained relatively high catalytic activity and structural stability, while the carbonaceous deposits, which come from the dissociation of CH₄ in the pulse reaction, occurred due to the low migration rate of lattice oxygen from the bulk toward the surface. A new dissociation–oxidation mechanism for this POM without gaseous oxygen is proposed based on the transient responses of the products checked at different surface states via both pulse reaction and switch reaction over the LaFeO₃ catalyst. In the absence of gaseous-phase oxygen, the rate-determining step of methane conversion is the migration rate of lattice oxygen, but the process can be carried out in optimized cycles. The product distribution for POM over LaFeO₃ catalyst in the absence of gaseous oxygen was determined by the concentration of surface oxygen, which is relevant with the migration rate of lattice oxygen from the bulk toward the surface. This process of hydrogen production via selective oxidation of methane by lattice oxygen is better in avoiding the deep oxidation (to CO₂) and enhancing the selectivity. Therefore, this new route is superior to general POM in stability (resistance to carbonaceous deposition), safety (effectively avoiding accidental explosion), ease of operation and optimization, and low cost (making use of air not oxygen).

Introduction

Hydrogen is both a clean energy source and an important raw material for the chemical and refining industries. The current chemical use of hydrogen is mainly for the production of methanol,^{1,2} ammonia,^{3,4} and for hydrotreatment in refineries.⁵ Most hydrogen production is currently obtained from natural gas, of which the main component is methane. The most important process is the catalyzed steam reforming of methane (SMR), in combination with the water–gas shift (WGS) reaction. SMR is strongly endothermic and operated at high temperature, low pressure, and a relatively higher ratio of steam to carbon.^{6,7} Partial oxidation of methane (POM) to H₂/CO (mildly exothermic) has recently attained more attention. In comparison with SMR, POM is more energy efficient, can be carried out at lower investment, and produces synthesis gas with a H₂/CO ratio of ca. 2, which is suitable for methanol and Fischer–Tropsch synthesis.⁸ Ni metal has been reported as the most promising catalyst system for commercialization; however, there are major drawbacks with Ni metal catalysts, such as phase

transformation,⁹ coke deposition, Ni sintering,¹⁰ and Ni losses.¹¹ In addition, POM usually occurs between gas-phase oxygen and methane, which limits the selectivity of CO and hydrogen due to complete oxidation of methane. There are also serious safety concerns related to the direct mixing of highly explosive feed gas (methane) with oxygen at high temperature.¹²

Other processes in the development for hydrogen production are thermochemical cycles,¹³ the steam–iron process,¹⁴ two-step cyclic processes with steam,¹⁵ methane decomposition,¹⁶ catalytic coal gasification,¹⁷ and combustion reforming.¹⁸ More processes, such as photochemical, photoelectrochemical, and photobiological processes, are also being explored.¹⁹ In this paper, a new process, which combines the WGS with a redox mode using lattice oxygen as the sole oxidant instead of gaseous oxygen in a fixed-bed reactor is reported. The process will eliminate the equipment for separate air compared to the partial oxidation and, thus, reduce the investment cost. In this process the lattice oxygen [O_L] selectively oxidizes methane from in situ formed H₂/CO. The redox process for methane conversion to H₂/CO in the absence of gaseous oxygen was performed in a microreactor with a LaFeO₃ perovskite catalyst, which exhibits excellent redox property, high oxygen mobility, and thermal stability. Due to their variable structure and chemical composition, LaFeO₃ perovskite-type oxides have so far attracted great

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Figure 1. Schematic system of analysis for periodical operation.

interest in catalysis for hydrocarbon and CO deep oxidation^{20–23} and catalytic combustion for NO_x and soot.^{24,25} However, LaFeO₃ perovskite-type oxides applied to the direct partial conversion of methane to synthesis gas free of gas-phase oxygen, combined with the WGS reaction for hydrogen production, have rarely been reported, and the role of lattice oxygen and the reaction mechanism for POM in the absence of gaseous oxygen over LaFeO₃ catalyst were not clearly identified. In the present paper, we used pulses and the transient responses of products to investigate the POM reaction over the LaFeO₃ catalysts. On the basis of the obtained results we identified and proposed the active sites and the reaction mechanism.

Experimental Section

Material Preparation. The LaFeO₃ oxides were prepared by the sol–gel method. Glycine was added into an aqueous mixed solution of the metal nitrates (La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O, >99%, Beijing Chemical Company) and kept at a ratio of NH₃/NO₃[−] = 1.05. Water was evaporated slowly from the mixed solution at 353–363 K until a viscous gel was obtained. The gel was then heated at 523 K for 30 min with a fast exothermic reaction, and the temperature was raised to 1173 K at a rate of 10 K/min in air. The yielded brown powder precursor was calcined at 1173 K for 10 h. The samples were crushed, ground, and sieved for experiment.

Material Characterizations. Phase analysis and lattice parameters were performed by X-ray powder diffraction (XRD) using a ShiDU XRD-6000 diffractometer with Ni-filtered Cu Kα radiation.

BET surface areas of the samples were measured by nitrogen adsorption/desorption at liquid nitrogen temperature, using a NOVA1200 gas adsorption analyzer.

Experimental Setup and Procedures. The experimental setup for a periodical operation is shown in Figure 1 and consists of three main parts: a gas flow system, two reactors with a temperature controller, and an online-detection mass spectrometer (AMETEC Quadlink 1000). The first quartz tube reactor, with an i.d. of Φ 6 mm and length of 400 mm, is placed in an electric furnace that can be operated in pulse reaction, redox cycles. The redox cycle was operated with a four-way valve, and pulse experiments were performed using a six-way sampling valve with a 0.75 mL quantitative tube. A measured volume of reactant is passed through the catalyst bed in a prescribed

Figure 2. Schematic of periodical operation.

amount, and the reactor effluent can be analyzed online by the quadruple mass spectrometer. A redox cycle consists of a reductive atmosphere (flow of a reductive gas at a set flow rate) followed by an oxidative atmosphere (flow of oxidative gas for a measured amount). Another reactor for the WGS reaction is filled with commercial Cu–Zn catalyst (Nanjing Chemical Industry Group).

The temperature inside the reactor bed is controlled by an AI-FUZZY temperature controller using a K-type thermal couple. The catalyst is packed in the middle of the reactor bed, and the free space of the reactor is filled with 20 to 40 mesh quartz particles. The quadruple mass spectrometer can detect eight mass channels simultaneously with the minimum dwell time of 3 ms.

Pulse Reactions. The pulse reactions were carried out in a fixed-bed reactor; the catalyst (0.2 g) was primarily heated in an Ar stream at 1173 K. A pulse of CH₄ gas was introduced with a six-port gas sampling valve equipped with quantitative tubes (0.75 mL), under a stream of Ar carrier gas. The total gas flow rate was maintained at 25 mL/min.

Sequential Redox Mode. Sequential optimized redox cycles were performed over the LaFeO₃ oxide for the production of H₂/CO in a fixed-bed reactor at 1173 K between reductive (CH₄/He) and oxidative atmospheres (O₂/Ar) (denoted as “redox”). The total gas flow rate was 25 mL/min. Ar/He was used as the dilution gas and tracer gas.

The different reaction products were detected by the mass spectrometer at $m/e = 2$ (H₂), $m/e = 15$ (CH₄), $m/e = 18$ (H₂O), $m/e = 28$ (CO), $m/e = 32$ (O₂), and $m/e = 44$ (CO₂). The CH₄, CO, H₂, and CO₂ pure pulses were injected in order to calculate the amount of CH₄, CO, and CO₂ on the catalysts taking into account a previous calibration of the mass spectrometer. The calibration of the mass spectrometer was carried out with standard gas mixtures (known composition). The cracking coefficients of methane, CO, and CO₂ have been determined and used to calculate their concentrations. The CO selectivity is defined as $\text{CO}/(\text{CO} + \text{CO}_2) \times 100\%$.

Results and Discussion

Hydrogen Production by Sequential Optimized Redox Cycles. As shown in Figure 2, the catalyst is located in a single reactor and the lattice oxygen [O]_L of the catalyst is the sole oxidant for the POM in situ, producing H₂/CO by a redox process. Typically, the WGS reaction is an integral part for the

hydrogen production and is used to convert CO in the synthesis gas to generate more H₂.

The main catalytic reactions involved in this process for hydrogen production are POM with lattice oxygen, recovery of lattice oxygen with gaseous O₂ or air, and WGS for CO removal. For the WGS reaction, related catalysts have been optimized for many years, so in this work we did not take more efforts on it.

As the lattice oxygen of the catalyst becomes depleted in the reduction reaction with methane, it should be replenished by gaseous oxygen in a subsequent reoxidation step. Thereafter, a new redox cycle could be started up again.

The reduction step:

The reoxidation step of the reduced catalyst:

WGS reaction:

Where:

$[\text{O}]_{\text{L}}$ lattice oxygen

$[\]_{\text{L}}$ oxygen vacancy

According to the Mars–Van Krevelen mechanism,²⁶ two independent steps should be distinguished as the CH₄ oxidation reaction and oxygen recovered by redox cycles:

where Pro are the products, O* are the oxidized sites, and [*] are the reduced sites. Separation of the reduction and oxidation steps is optimized for the operating conditions of each step. A sweeping step with inert gases between the reduction and oxidation steps for desorption of adsorbed oxygen on the surface is involved.

The redox experiments over 0.25 g of LaFeO₃ catalyst were tested at 1173 K isothermal conditions, in atmospheric pressure between O₂/Ar (11% O₂ by mol, 10 s) and CH₄/He (11% CH₄ by mol, 30 s). The reaction temperature was determined previously to produce a level of conversion suitable for study. Ar/He was used as the dilution gas and tracer gas, and the results are shown in Figure 3.

Figure 3 indicates the reactants and products formation responses during the cyclic reactions between O₂/Ar oxidation for 10 s and CH₄/He reduction for 30 s over the LaFeO₃ catalyst at 1173 K. In the first cycle, the methane was oxidized totally first by very reactive oxygen species over fresh LaFeO₃ catalyst to form CO₂ and H₂O, and then CO and H₂ were detected when the concentration of very reactive oxygen species declined. When the lattice oxygen consumed at reductive atmospheres (CH₄/He) was restored partially at oxidative atmospheres for a short time (10 s), the oxidation level of the catalyst may not reach the initial state, while most of the oxygen species, which can react with CH₄ to form H₂ + CO, can be regenerated again by gaseous oxygen during the reoxidation step. From the second redox cycle to the sixth redox cycle, the conversion enhanced slowly, and CO₂ was not measured, while the selectivity to CO

Figure 3. Reactants and products formation responses of optimized redox operation over LaFeO₃ oxide at 1173 K isothermal conditions.

increased, and H₂ + CO were the dominant products. But from the seventh cycle, the amount of CO₂ declined to a lower level and increased with redox number, while the selectivity to CO remained at a higher level (>96%). The CH₄ conversion remained at a level of 60–70% during the whole redox experiments, but it decreased slightly with the increase of cyclic number; it is observed from the change of CH₄ intensity. The ratio of H₂/CO is about 1.93 and close to the stoichiometric ratio of the POM. The results of reoxidation at 1173 K isothermal conditions on the reduced LaFeO₃ catalyst show that the LaFeO₃ oxide has a high reactivity toward the oxygen, which is not detected during the redox experiment. CO₂ or CO originating from carbonaceous deposits on the catalyst surface was not observed at oxidative atmospheres of redox cycles. This indicates that the carbon species over active sites from the dissociation of methane can be consumed completely to form synthesis gas at the appropriate reaction condition.

These results indicate that the less reactive oxygen species for the CO formation can be regenerated, while the very reactive oxygen species for the CO₂ formation is recovered hardly at appropriate condition. The LaFeO₃ catalyst was exposed to extremely high temperatures exceeding 1173 K and experienced fluctuation between reductive and oxidative (redox) atmospheres during the 80 redox cycles, which exhibited relatively high catalytic activity and structural stability from XRD characterization (as shown in Figures 3 and 4), which was observed by Ciambelli et al.,²² but the quantity of CO₂ increased with redox number, and the appearance of a deactivation phenomena may be due to the change of the redox properties of Fe. The reduction of the iron cations of perovskite to metallic iron was observed over 873 K by Frank et al.²⁷ The sintering of iron oxide was found by Li and Shen²⁸ and Mccart and Wise²⁹ when the temperature exceeds 1173 K; their experimental results are

Figure 4. Comparison of XRD profiles over pre- and postreaction LaFeO₃ catalyst.

Figure 5. Methane pulse reaction over fully oxidized LaFeO₃ catalyst at 1173 K.

similar to our observation, which confirms the reason of deactivation phenomena.

According to the results above, it is reasonable that methane is oxidized by the lattice oxygen species and then can be replenished by the oxygen of the atmosphere. Under steady conditions, some vacant sites could be reduced by feed gas methane, and some of the reduced LaFeO₃ catalyst could be reoxidized by molecular oxygen, which is the main route for replenishing the lattice oxygen. So it is possible that POM to H₂ + CO by using the lattice oxygen of oxides instead of molecular oxygen over a LaFeO₃ catalyst can occur by a redox mode.

Pulse Reaction. For this reaction, the 20 pulses of methane were injected continuously over LaFeO₃ catalyst. The catalyst was the fresh sample after calcination and had been pretreated in situ with pulses of oxygen at 1173 K to ensure complete oxidation. There was no reoxidation step between the two continuous pulses of methane.

The product distributions of CH₄ continuous pulses over LaFeO₃ catalyst at 1173 K isothermal conditions are shown in Figure 5, and the CH₄ conversion is illustrated in Figure 6. It is obvious that CH₄ conversion for the first pulse is ~50%; H₂ and CO are the dominant products with a CO selectivity of 87% (the selectivity to CO₂ was low, 13%). After the second pulse, the selectivity of CO₂ decreases to zero and CO selectivity increases sharply. The higher conversions of methane are

Figure 6. Methane conversion vs pulse number over fully oxidized LaFeO₃ catalyst at 1173 K.

maintained at the level of 80% with the increasing pulse number (as shown in Figure 6). Obviously, the amount of oxygen can not only be ascribed to the surface oxygen, because of the amount of oxygen at the first surface layer on the basis of the low BET surface area (ca. 6 m²/g oxide calcined at 1173 K). Therefore, it is clear that the bulk lattice oxygen of LaFeO₃ oxide should participate in the partial oxidation of CH₄ to H₂ + CO. Exposure of LaFeO₃ oxides to a reduced atmosphere can generate oxygen vacancies due to the loss of lattice oxygen and reduction of the oxidative state of the Fe ion simultaneously, providing pathways of oxygen transport through the lattice,³⁰ which decrease the resistance of oxygen migration and lead to enhancement of oxygen diffusivity. The relationship between the rate of oxygen migration and concentration of oxygen vacancies has been confirmed by Rossetti and Forni.³¹ It can be speculated that H₂ + CO is generated with a constant rate on the regular surface sites including those on the exposed surface of microdomains. Since there was no gas-phase oxygen present in the system, it implies that the surface oxygen species were from lattice oxygen, which would originate from the reduction of Fe³⁺ to Fe²⁺ and further to metallic Fe in LaFeO₃ oxide.³² As the number of pulses is increased, the catalyst surface becomes more and more reduced and the synthesis gas formation rises, while the CO₂ formation tends toward zero. Upon further pulsing, dissociation of CH₄ resulted in a higher H₂ signal, and carbon deposition occurred on the LaFeO₃ surface due to the lower concentration of oxygen species around the dissociative C* on the active sites.

After 20 pulses of CH₄, only CO was formed during pulsing with oxygen, as shown in Figure 7. In the pulse reaction, only H₂ was detected and no H₂O could be found. A large amount of CO was produced for the three pulses of O₂, while no CO₂ was detected. These could be the oxidation of the carbonaceous deposits on the catalyst surface, which originated from the methane dissociation. This is similar to the observations for LaFeO₃ perovskite reported by Belessi et al.³³ and Liu et al.³⁴ Moreover, in the first seven oxygen pulses, gaseous oxygen was completely consumed, which shows that LaFeO₃ catalyst has a high reactivity toward with gaseous oxygen. Oxygen was not detected until the eighth pulse. Constant oxygen signals were observed after the ninth pulse, and no products were detected. Obviously, the total amount of oxygen atoms in O₂, CO, and CO₂ detected in the effluent was less than the oxygen pulsed for the first 12 pulses. Reoxidation includes the surface adsorption of oxygen and the migration of adsorbed oxygen to

Figure 7. Oxygen pulse reaction over reacted LaFeO₃ catalyst at 1173 K.

Figure 8. Transient responses of products switched from Ar to CH₄ over fully oxidized LaFeO₃ catalyst at 1173 K.

oxygen vacancies in the bulk. The missing oxygen was apparently changed into the oxygen vacancy lattice position in the catalyst via reoxidation of the catalyst.

With a constant rate of the CO release, the rate of lattice oxygen migration is supposed to be the rate-determining step, rather than the activation of methane on the surface sites for the partial oxidation reaction in the absence of gaseous oxygen. The carbonaceous deposits, coming from the dissociation of CH₄, accumulated due to the low migration rate of lattice oxygen from the bulk toward the surface over the LaFeO₃ catalyst.

Role of Oxygen Species and Reaction Mechanism over LaFeO₃ Catalyst without Gaseous Oxygen. The reaction between the lattice oxygen of the LaFeO₃ catalyst and methane without gaseous oxygen was also carried out by transient response of the products at different surface states in order to investigate the role of lattice oxygen and the reaction mechanism for methane conversion at 1173 K isothermal conditions. All the results are shown in Figures 8–10.

The product profiles in the switch reaction from Ar to CH₄ on the fully oxidized LaFeO₃ catalyst are shown in Figure 8. There is a delay between H₂, CO and H₂O, CO₂. With the concentration of surface oxygen declined, H₂ and CO appear to be produced over the LaFeO₃ catalyst in the absence of gaseous oxygen. We analyzed the evidence for the participation of lattice oxygen in the oxidation. The evolution of products stems from exposing the oxidized catalyst to methane. The CO₂ and H₂O were formed first, then CO and H₂ were detected for

Figure 9. Response curves of products for the CH₄ pulse reaction on fully oxidized LaFeO₃ catalyst at 1173 K.

Figure 10. Product profiles obtained switch CH₄ → Ar/O₂ → CH₄ over partially oxidized LaFeO₃ catalyst at 1173 K.

the switch reaction over the fully oxidized LaFeO₃ catalyst. But the intensity of CO₂ did not decline immediately when the CO began to be detected. This indicates that the CO and H₂ are not the products of CH₄ reforming with CO₂ and H₂O. The results in Figure 9 indicate that the products (CO₂, CO, and H₂) are detected by the mass spectrometer with a various delay compared to that of CH₄. We define the time as the induction period for methane dissociation. The responses of CO and CO₂ are detected simultaneously, but they are delayed compared to that of H₂. The CH_x* or C* species react further with lattice oxygen to form CO and CO₂ through two different surface reaction routes which compete with each other, while adsorbed H atoms from the dissociation of methane may combine to form hydrogen and desorb easily to the gas phase from the active sites. Figure 10 shows the response profiles of products obtained during the switch CH₄ → Ar/O₂ → CH₄ over partially oxidized LaFeO₃ catalyst at 1173 K. The oxygen species of the reduced-state LaFeO₃ is recovered partially by gaseous oxygen. As compared with fully oxidized LaFeO₃ catalyst (Figure 8), water was shifted toward longer residence times over partially oxidized LaFeO₃ catalyst. The amount of CO₂ decreases obviously. These can be related to the surface state, which strengthens absorption of H₂O with the active site and decreases the concentrations of surface-active oxygen species. The significant differences in the product distribution of the POM reaction over fully oxidized and partially oxidized LaFeO₃ catalysts can be well related to the difference in the concentration of surface oxygen species over the LaFeO₃ catalysts. The pulse responses of pure H₂ and pure CO indicated that the reaction between H₂ and lattice

oxygen over partially oxidized surface of LaFeO₃ catalyst hardly occurred, while CO can be oxidized totally to CO₂ with lattice oxygen at 1173 K. The experimental results with methane pulses (as shown in Figures 5 and 7) also provide some insight into the mechanism of POM. Indeed, in the reaction of pure methane and lattice oxygen, a noticeable amount of carbon was deposited over the LaFeO₃ catalyst (as shown in Figure 7). Of course, the generation of the surface carbon originates from methane and follows the dissociation $\text{CH}_{4,s} \rightarrow \text{CH}_{x,s} \rightarrow \text{C}_s$. When the concentration of surface oxygen species is high (as shown in Figure 8), the main products are CO₂ and H₂O, while for low concentrations of surface oxygen species (as shown in Figure 10), the main products are CO and H₂. These are relevant with the concentration of surface oxygen species around the dissociative C* on active sites. For the LaFeO₃ catalyst, a strong increase in the reduction rate with time indicates that this process proceeds through a growth of nuclei of a new reduced phase (probably metallic iron and/or its carbide). Sadykov et al.³⁵ reported that a new reduced phase was caused by a low rate of the oxygen migration by bulk mobility of oxygen in the lanthanum ferrite lattice, which favors a rapid formation of the reduced nuclei at the surface. From the experimental results, the H₂ + CO formation was favored by the rapid dissociation of methane, which apparently proceeds easier on the reduced surface containing the metal/carbide clusters or nuclei.

Integrated with the results of the pulse reaction, transient responses, and redox cycle, combined with the above literature,^{27,32,35} the reaction mechanism can be expressed as follows:

Reduction step:

Oxidation step:

Methane is dissociatively chemisorbed in step 1. Dissociation is depicted as two steps although it probably takes place stepwise. As mentioned in the Finocchio et al.'s work,³⁶ in the case of a more stable molecule like methane, the dissociation of the first C–H bond requires considerably higher energy than the dissociation of a C–H bond in the formed surface species. Adsorbed H atom may combine to form hydrogen and easily desorb (step 2). The chemisorbed carbon species is either oxidized to CO by lattice oxygen (step 3), or oxidized totally to CO₂ (step 4), or forms an inactive carbon (step 1). The CO and CO₂ originate from similar carbon-containing species, but the reactions compete with each other. The above scheme, the so-called dissociation–oxidation mechanism, is plausible, and more work is still needed to further confirm the individual steps and the intermediate species.

According to the above scheme, the product distribution for the POM reaction over LaFeO₃ catalyst was determined by the concentration of surface oxygen species, which is affected by the migration rate of oxygen from the bulk toward the surface. The catalyst development for methane partial oxidation using lattice oxygen instead of gaseous oxygen must dedicate to improve the migration rate of oxygen, enhance oxygen exchange

capability, increase the active sites for methane dissociation and optimize the redox cycle for hydrogen production.

Conclusions

Combined with WGS, a redox cycle process for hydrogen production in a fixed-bed reactor via a switch reaction is presented in this paper. In the redox cycle process, CH₄ and O₂ are periodically brought into contact with the catalyst by making use of lattice oxygen existing in the solid oxide materials instead of gaseous oxygen as the sole oxidant for POM. It was found that under an appropriate reaction conditions, methane can be oxidized to CO and H₂ with a selectivity higher than 95% by the lattice oxygen of LaFeO₃ perovskite oxide (as an oxygen donor material), and the consumed lattice oxygen can be recovered in a reoxidation procedure by a redox operation. It was proved that POM to H₂ + CO by using the lattice oxygen of the catalyst is possibly applicable. The carbonaceous deposits coming from the dissociation of CH₄ in the pulse reaction were formed due to the low migration rate of lattice oxygen from the bulk toward the surface, which is supposed to be the rate-determining step, rather than the activation of methane on the surface-active sites. The transient responses of products at different surface states in the pulse and switch reaction over the LaFeO₃ catalyst clearly demonstrate that POM over LaFeO₃ proceeds as a dissociation–oxidation mechanism. The product distribution for POM over LaFeO₃ catalyst in the absence of gaseous oxygen was determined by the concentration of surface oxygen, which is relevant with the migration rate of lattice oxygen from the bulk toward the surface. For hydrogen production, this new route is superior to POM in terms of stability, safety, ease of operation, optimization, and cost efficiency.

Acknowledgment. Financial funds from the Chinese Natural Science Foundation (Project Nos. 20306016, 20322201) and the National Basic Research Program of China (2004CB217808, 2004CB719500) are gratefully acknowledged.

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