

Article

Pulse Microcalorimetry Study of Methane Dry Reforming Reaction on Ni/Ceria-Zirconia Catalyst

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Abstract: For Ni/CeZrO catalyst prepared in supercritical isopropanol main features of methane dry reforming reaction mechanism were studied by the pulse microcalorimetric technique. The reaction scheme is described by a step-wise redox mechanism with independent stages of CH₄ transformation on Ni/support interface producing syngas with participation of support oxygen bridging species (the rate-limiting stage) and fast reoxidation of support sites by CO₂ yielding CO regenerating reactive oxygen species.

Keywords: synthesis in supercritical alcohol; ceria-zirconia; pulse microcalorimetry; methane dry reforming; mechanism

1. Introduction

Catalysts consisting of metal nanoparticles (Pt, Ru, Ni + Ru) deposited on the surface of fluorite-like (Ln–Ce–Zr–O) oxides with high surface/lattice oxygen mobility and reactivity demonstrate high activity and stability to coke formation in dry methane reforming [1–5]. This is explained by the bifunctional scheme of the reaction mechanism including activation of CH₄ on metal sites, CO₂—on oxide sites with the subsequent rapid transfer of oxygen species to the metal-support interface, where they interact with activated CH_x species producing syngas [6]. However, for undoped ceria-zirconia oxides with loaded Ni there is still no direct evidence of such a mechanism, and the question remains what is the nature of the rate determining stage. Another question concerns the activation of reagents on these catalysts being really independent or conjugated. Indeed, for traditional catalysts such as Pt, Ni, and Co supported on alumina, the pulse microcalorimetric studies by Bychkov et al. [7,8] have reliably demonstrated that CO₂ is activated by direct interaction with carbon atoms on the surface of metal, which is the slowest step of dry reforming. For the Ni/SiO₂ catalyst, the TAP (Temporal Analysis of Products) studies of Schuurman and Mirodatos have shown that CO₂ is activated by direct dissociation on Ni atoms, whereas the rate-limiting step is the interaction between C and O adsorbed on Ni [9]. Consequently, depending on the support nature even for the same metal, different ways of CO₂ activation can take place. The evaluation of the conversion of reagents in mixed and separate pulses fed to a steady-state catalyst is a conventional approach to elucidate the reaction mechanism of catalytic red-ox reactions [7–13]. However, it has not yet been used to study dry reforming of methane on catalysts consisting of inexpensive Ni deposited on undoped mixed ceria-zirconia oxides with a high uniformity of the spatial distribution of Ce and Zr cations providing a high mobility and reactivity of the surface/bulk oxygen. In this work, for Ni/CeZrO catalyst prepared by a novel continuous preparation technique in supercritical alcohol medium [14] pulse microcalorimetric studies were conducted to determine the main features of the reaction mechanism of methane dry reforming.

2. Results

2.1. Catalyst Characterization

According to XRD (X-ray diffraction) data presented in [14], the calcined sample represents CeO₂–ZrO₂ solid solution of pseudocubic fluorite phase referred to as the Fm3m space group. The spherical-shaped particles of ceria-zirconia catalyst with size of 100–500 nm consist of smaller crystallites with sizes up to 22 nm. Specific surface area of the catalyst is 9 m² g^{−1}. For the calcined sample, NiO nanoparticles with average size ranging from 23 to 28 nm were revealed according to TEM (Transmission electron microscopy). It is worth noting that these values are somewhat greater than those estimated by X-ray diffraction (15 nm). This may be caused by the presence of bulk defects in NiO crystallites resulting in a decrease of the effective X-ray crystallite size.

2.2. Pulse Microcalorimetry at 973 K

The temperature of dry reforming of methane was chosen in order to obtain either full (973 K) or nearly a half (773 K) conversion of methane.

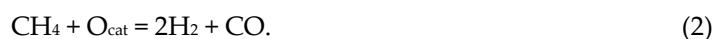
The experimental sequence was as follows:

1. Continuous flow of reaction mixture (5% CH₄ and CO₂) in He at 973 K for 30 min. After that small (pulse volume 0.85 mL) probing pulses and big (pulse volume 3.6 mL) pulses of reaction mixture were fed into the reactor by turns. Mixtures of products from small pulses were analysed by GC (gas chromatography), whereas products from big pulses were not analysed due to GC column overloading. Big pulses were used to achieve steady-state of the catalyst more quickly. It is important to note that the use of alternating small and big pulses was equivalent to the use of only small pulses, and the achieved steady state of the catalyst depended only on the temperature of the reactor and composition of the pulse.
2. Pulses of 5% CH₄ in He (pulse volume 0.85 mL).
3. Small (pulse volume 0.85 mL) probing pulses and big (pulse volume 3.6 mL) pulses of reaction mixture.
4. Pulses of 5% CO₂ in He.
5. Small (pulse volume 0.85 mL) probing pulses and big (pulse volume 3.6 mL) pulses of reaction mixture.
6. Pulses of CO in He.

Figures 1 and 2 show conversions of methane and CO₂, the mass balance as well as ratios of hydrogen and CO, including mole of products per mole of converted methane estimated by GC analysis. It should be noted that the mass balance in the entire experiment was close to unity, which indicates the reliability of the data obtained. During the first pulse of the RM (reaction mixture CH₄ + CO₂), additional H₂ and CO₂ super-stoichiometric emissions occurred, associated with the participation of the oxygen of the catalyst, which is in a more oxidized state compared to the stationary state of the catalyst. Starting with the 4th pulse of the RM, the conversion of CO₂ stabilizes at the level of 0.9 at full conversion of methane, which indicates the achievement of a steady state of the catalyst in methane dry reforming reaction:



During supply of methane pulses in the absence of CO₂ synthesis gas is produced but the ratio of H₂ to CO was about 2 with the total conversion of methane, which is due to the reaction of formation of synthesis gas with the participation of catalyst oxygen O_{cat} in accordance with equation:



Then the catalyst was again brought to the stationary state using RM pulses (pulses from 13 to 16) and then pulses of CO₂ were fed, during which a decrease in the degree of CO₂ conversion, characterizing the process of reoxidation of the stationary-state catalyst was observed.

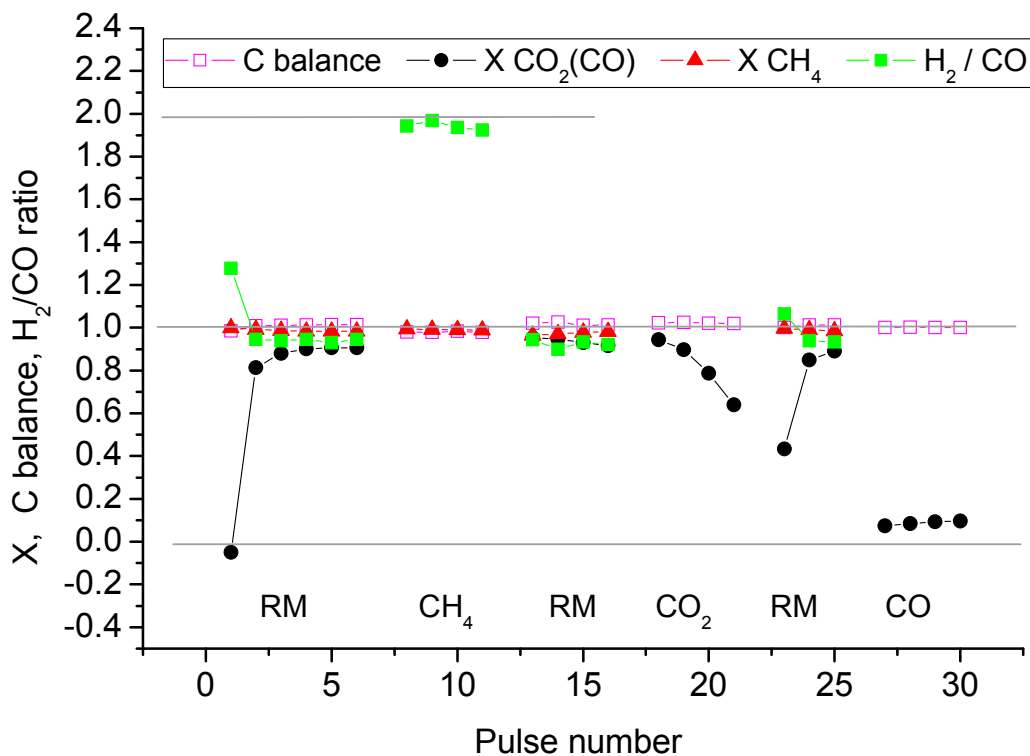


Figure 1. Conversions of reagents and products characteristics in series of pulses at 973 K.

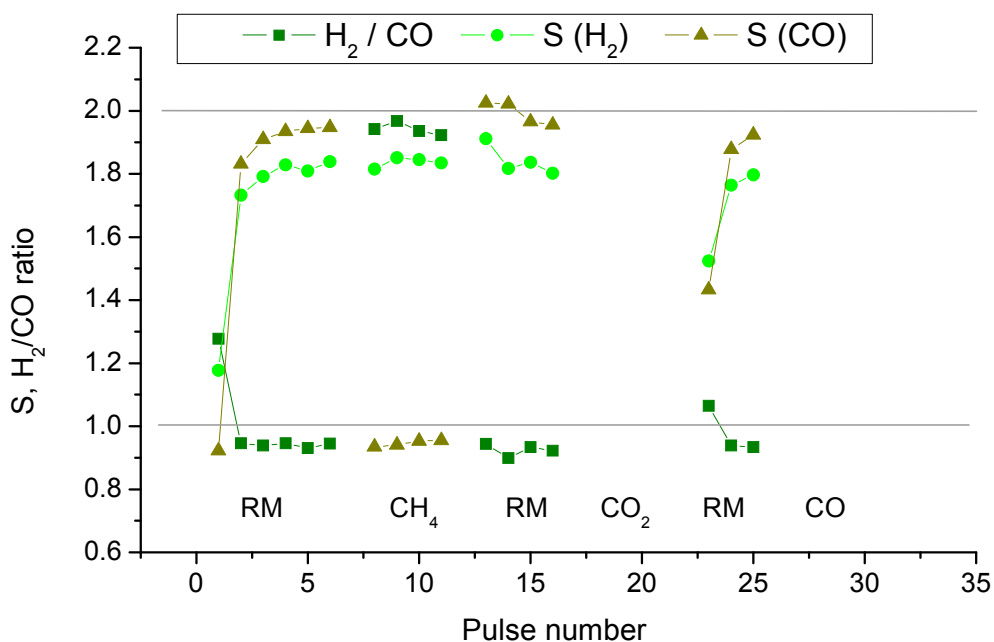


Figure 2. Product selectivities and syngas composition in series of pulses at 973 K.

Figure 3 shows the values of the measured heat effects depending on the pulse. It is clearly seen that when the pulses of RM (CH₄ + CO₂) are fed to the stationary-state catalyst, the observed heat effects are identical to the standard value of the enthalpy of methane dry reforming reaction ~260 kJ/mol. In a series of methane pulses (pulses from 8 to 11), the heat effect shifts even more to the endothermic region, which is explained by the involvement of mobile oxygen of the catalyst. Estimated values of the oxygen bonding strength (heat of O₂ chemisorption) are ~655 kJ/mol O₂.

When CO₂ pulses were supplied to the stationary-state catalyst, a pronounced exothermic effect was observed due to reoxidation of the catalyst regenerating the surface oxygen species. The bonding strength of these oxygen species estimated from these experiments is ~650 kJ/mol O₂, which is consistent with the value obtained above. Moreover, when CO pulses were applied to the catalyst in a stationary state, a partial reduction of ceria-zirconia surface took place with CO conversion less than 10% in each pulse, and the bonding strength of oxygen species was found to be 630–670 kJ/mol O₂.

Since conversions of reagents in their mixed and separate pulses are very close, this suggests that mechanism of CH₄ dry reforming on the catalyst with a high oxygen mobility can be described by the redox scheme, in which activation of methane and carbon dioxide occurs independently.

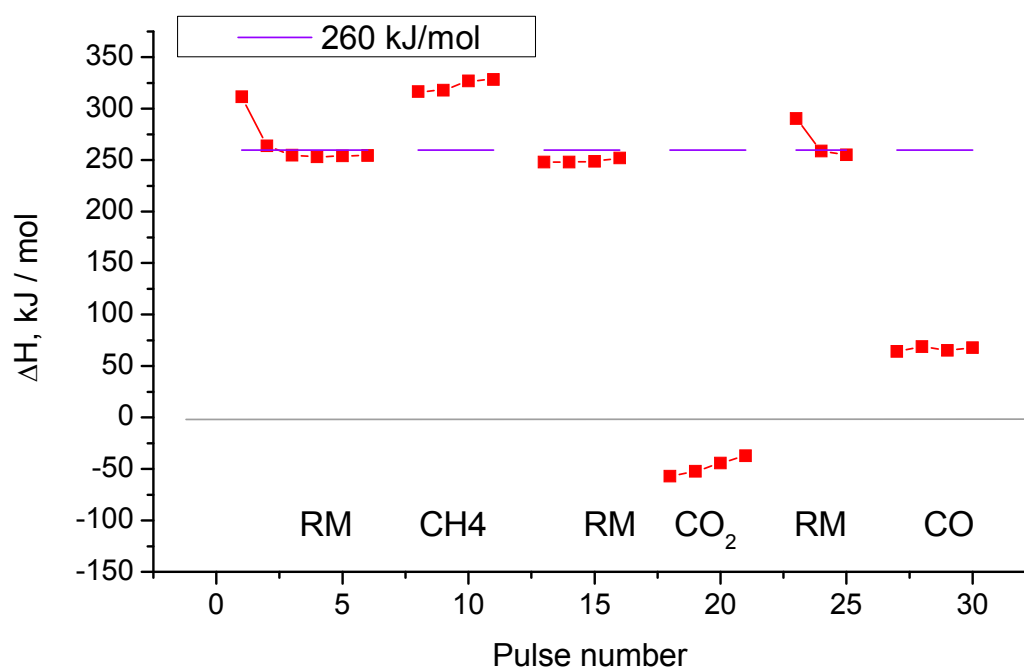


Figure 3. Measured heat effects during pulses of different compositions at 973 K.

2.3. Pulse Microcalorimetry at 773 K

The next stage of this research was the study of the reactions taking place in the system with incomplete conversion of reagents. It is well known that a decrease in temperature or contact time promotes a decrease in conversion. So, the experimental results below were obtained at 773 K. The general procedure was as follows:

- 1) Continuous flow of reaction mixture (5% CH₄ and CO₂) in He at 773 K for 30 min. After that small (pulse volume 0.85 mL) probing pulses and big (pulse volume 3.6 mL) pulses of reaction mixture were fed into the reactor by turns. Analysis method was the same as at 973 K described above.
- 2) Pulses of 5% CO₂ in He.
- 3) Small (pulse volume 0.85 mL) probing pulses and big (pulse volume 3.6 mL) pulses of the reaction mixture.
- 4) Pulses of 5% CH₄ in He (pulse volume 0.85 mL).
- 5) Pulses of 5% CO₂ in He.

Figures 4 and 5 show conversions of methane and CO₂, the mass balance as well as the ratios of hydrogen and CO including selectivities defined as mole of products per mole of converted methane calculated from the chromatographic analysis data. It should be noted that, like at a higher temperature, the mass balance in the entire experiment was close to unity, which indicates the reliability of the data obtained. During the first pulse of the RM, there was an excessive release of H₂

and CO₂, associated with the participation of the oxygen of the catalyst, being in a more oxidized state compared with the stationary state of the catalyst. Starting with the 2nd pulse of the RM, conversions of reagents are stabilized. Further, CO₂ pulses were fed to the catalyst in a steady state, during which a gradual decrease in the degree of conversion of CO₂ was observed due to the reoxidation of the steady-state catalyst.

After that, the catalyst was again brought to a steady state and methane pulses were fed in the absence of CO₂, while the synthesis gas was released, but the ratio of H₂ to CO was about 2.4 with a gradual decrease to 2 with a lowering methane conversion from 60% to 50%, which is associated with the reaction of formation of the synthesis gas with the participation of the catalyst oxygen O_{cat} in accordance with Equation (2). The decrease in methane conversion is associated with the depletion of the catalyst mobile oxygen O_{cat}.

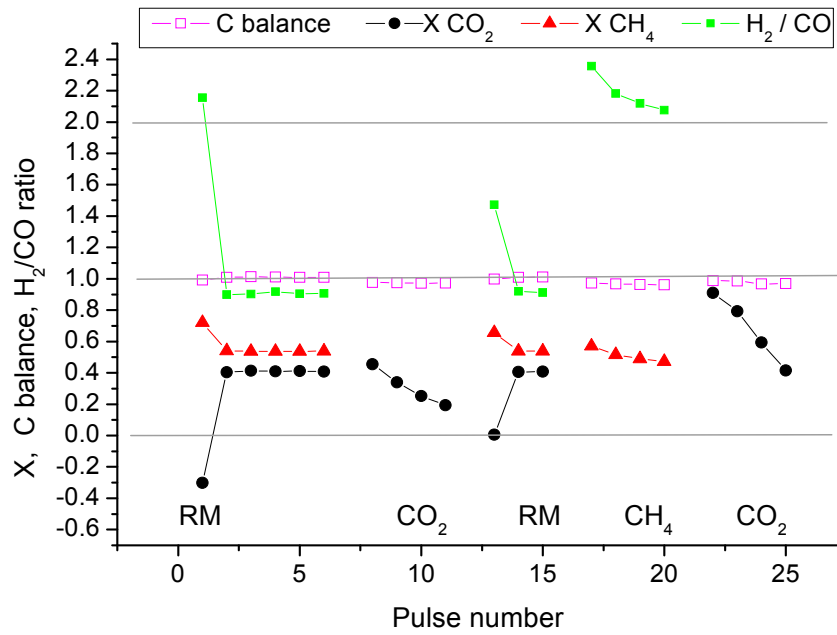


Figure 4. Conversions of reagents and products characteristics in series of pulses at 773 K.

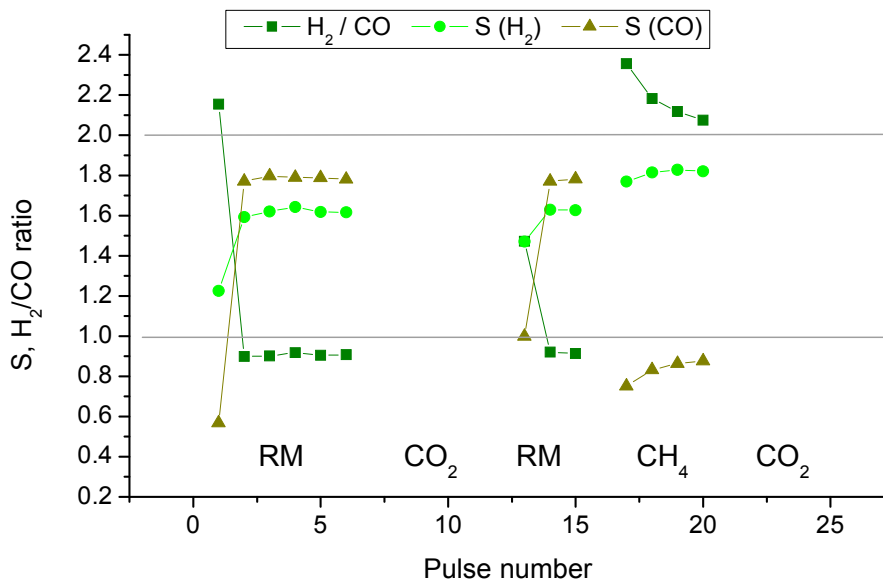


Figure 5. Product selectivities and syngas composition in series of pulses at 773 K.

Figure 6 shows the values of the measured heat effects depending on the pulse composition. The data obtained with incomplete conversions of reagents are consistent with those obtained previously at full conversion. Thus, when pulses of the RM ($\text{CH}_4 + \text{CO}_2$) are fed to the catalyst in the stationary state, the observed heat effects are identical to the standard value of the enthalpy of methane dry reforming reaction (1), about 260 kJ/mol. The exothermic effect when CO_2 pulses are fed to the stationary catalyst is due to its reoxidation, the surface oxygen bonding strength is 650 kJ per mol O_2 , which agrees with the values obtained above. In a series of methane pulses (pulses from 16 to 19), the thermal effect shifts to the endothermic region in comparison with the tabulated value of methane dry reforming reaction, which is explained by participation of the surface oxygen yielding synthesis gas according to reaction (2). The heat of oxygen chemisorption for the steady-state catalyst determined from the measured heat effects at 773 K, was about 650 kJ per mol O_2 . All the observed regularities were similar for the results obtained at 823 K, which are not shown for brevity.

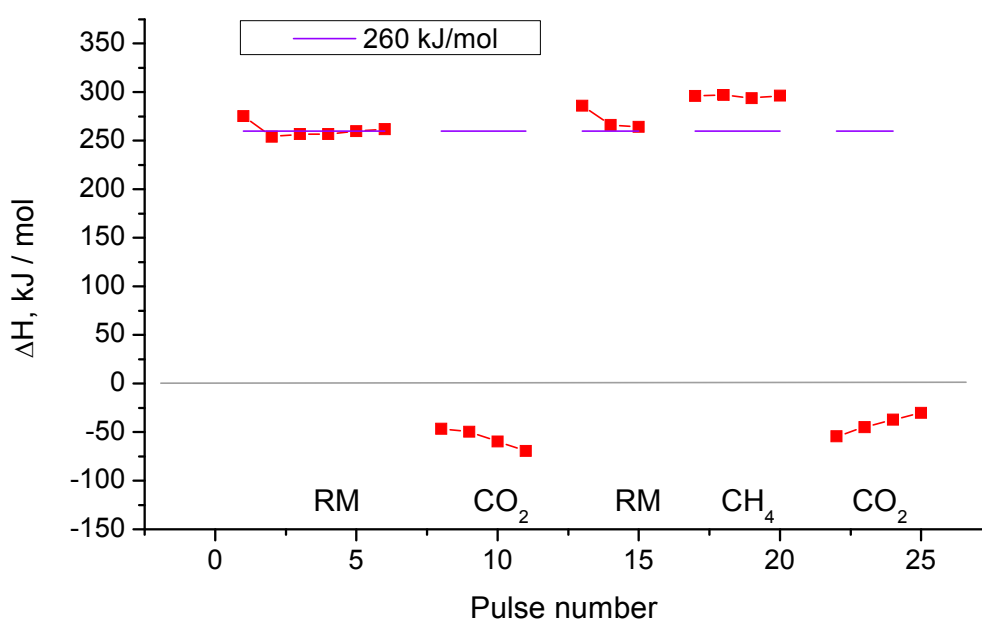


Figure 6. Measured heat effects during pulses of different compositions at 773 K.

As to the comparison of the results obtained at 973 and 773 K, the differences obtained in these two series of experiments consist mainly in conversions of reagents and in H_2/CO ratio which is caused by the temperature dependence of WGS reaction. The measured values of the thermal effects of chemisorption of oxygen coincide with each other and with the data obtained earlier for fluorite-like and perovskite-like catalysts [13].

Additionally, experiments were performed with a modified sequence of pulses. As shown in Figure 7, after achieving the steady-state with RM pulses, CO_2 pulses were applied followed by methane pulses. There were no pulses of the reaction mixture between pulses of CO_2 and methane. The CO_2 conversion in CO_2 pulses is slowly decreasing, which is due to the oxidation of the stationary catalyst. When methane pulses are fed, its conversion firstly reaches 0.8 and gradually decreases below the stationary level, which is associated with the consumption of mobile oxygen of cerium-zirconium oxide.

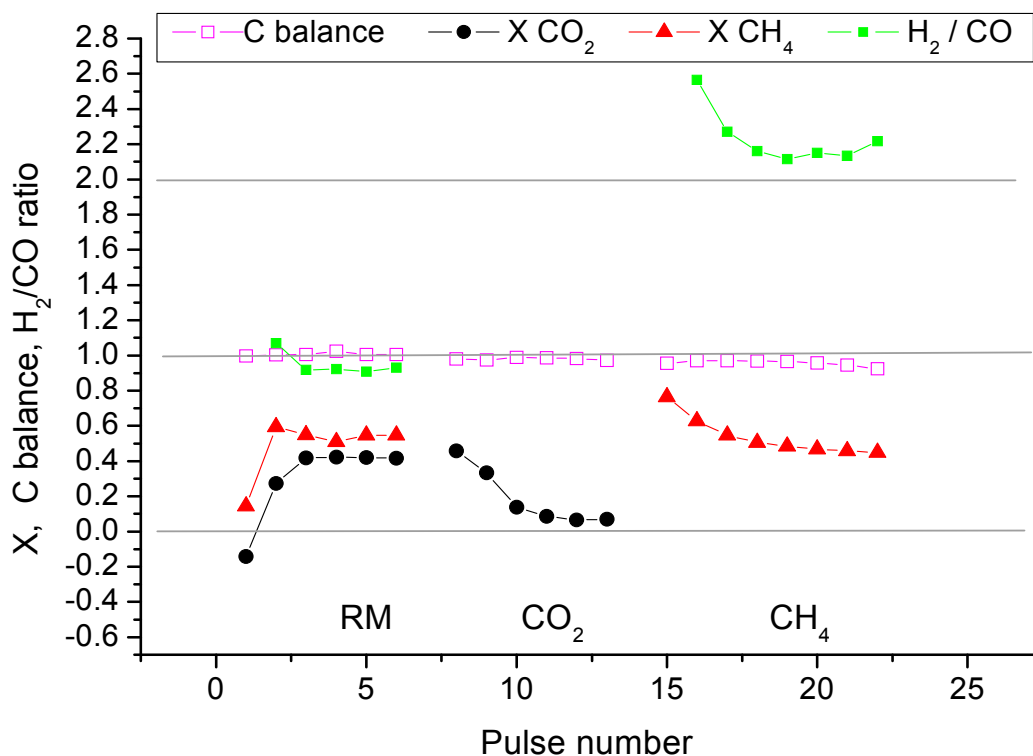


Figure 7. Conversions of reagents and products characteristics in series of pulses at 773 K.

As can be seen from Figure 8, the amount of hydrogen is approximately equal to the amount of CO in terms of converted methane in the case of RM pulses, which corresponds to the stoichiometry of the methane dry reforming reaction. During RM pulses the amount of H₂ is slightly less than CO because of the reverse water gas shift reaction. In methane pulses, the ratio of hydrogen to CO is much higher exceeding 2, which is explained by the oxidation reaction of methane with mobile oxygen of the catalyst. In this case, the quantity of products tends to decrease after the twentieth pulse, which is due to the consumption of the reactive/mobile oxygen species.

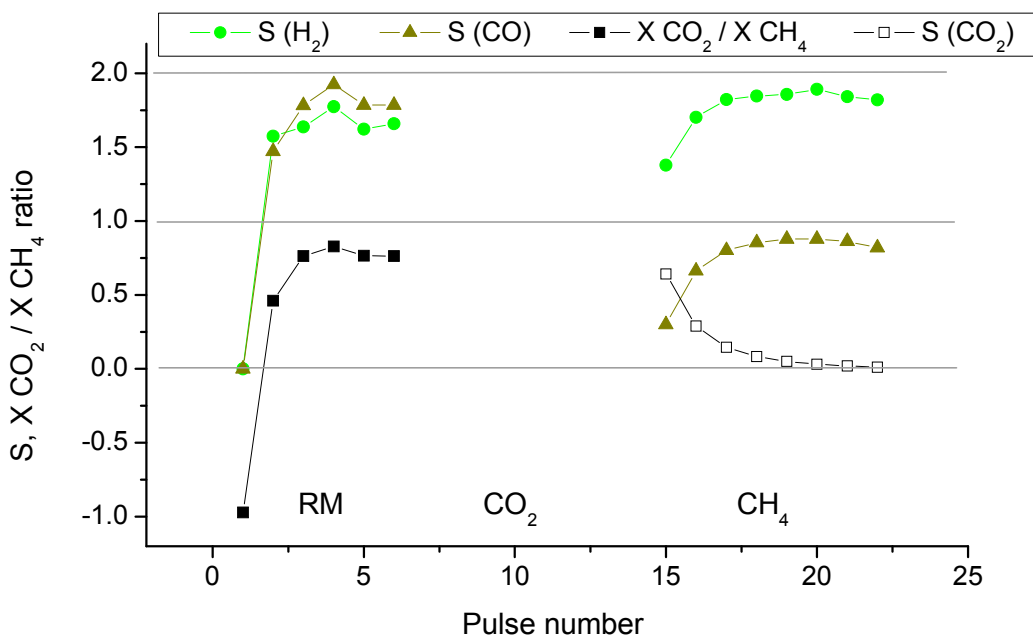


Figure 8. Product selectivities and conversions ratio in a series of pulses at 773 K.

Figure 9 shows the heat effects for this series of experiments. It is clear that the heat effect when the RM pulses are fed is exactly equal to the standard enthalpy of methane dry reforming reaction. However, when feeding methane pulses, the thermal effect is more endothermic not depending on the degree of methane conversion, which is due to participation of the catalyst’s oxygen.

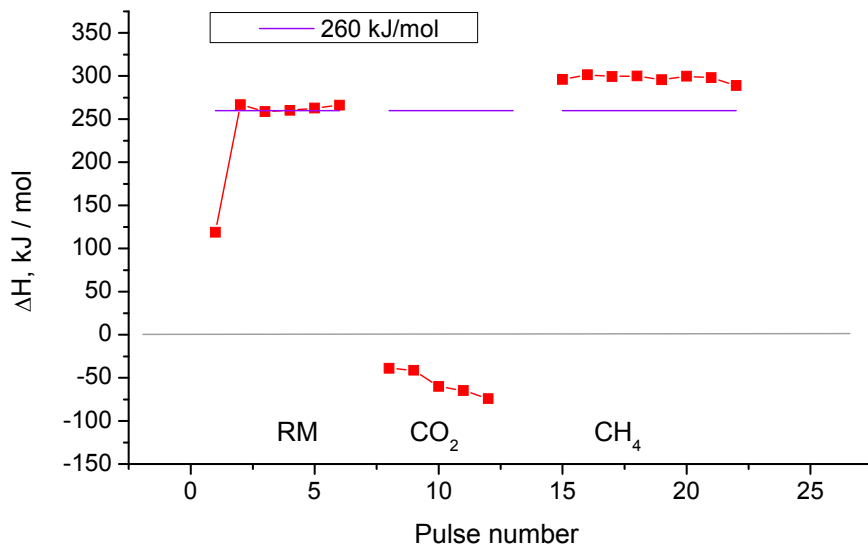


Figure 9. Measured heat effects during pulses of different compositions at 773 K.

Experiments were also carried out to oxidize the steady-state catalyst with pulses of oxygen in He. As can be seen from Figure 10, oxygen was completely absorbed by feeding seven pulses with a volume of 0.85 mL. To accelerate the oxidation process, two large pulses with a volume of 3.6 mL were then fed, the first of which was completely absorbed. In the course of subsequent pulses, the oxygen uptake gradually decreased to zero. The total amount of chemisorbed oxygen was 2.85×10^{-5} moles O_2 or 11.2 monolayers indicating participation of sub-surface oxygen. The thermal exo effect is approximately constant and does not depend on the volume of the pulse, as can be seen from Figure 11.

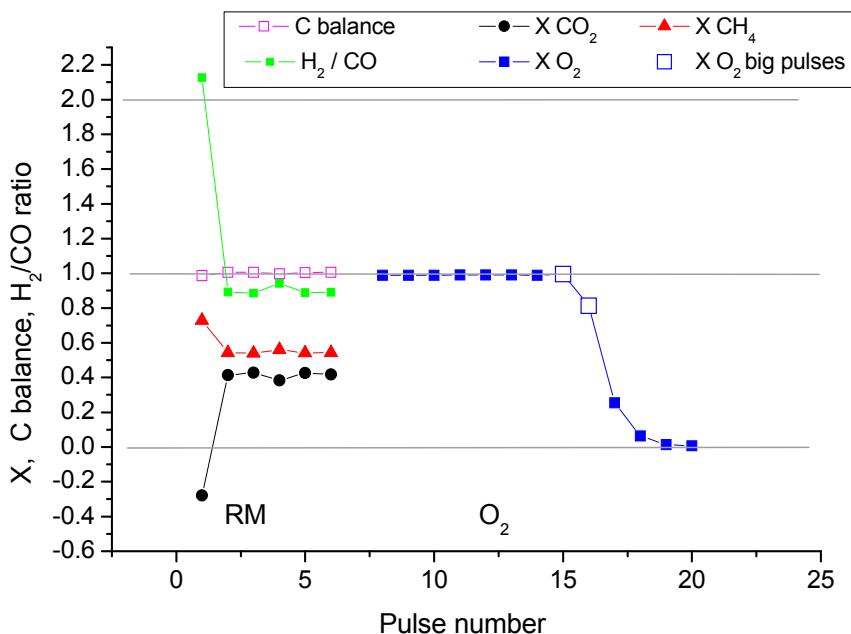


Figure 10. Conversions of reagents and product characteristics in series of the reaction mixture pulses followed by O₂ pulses at 773 K.

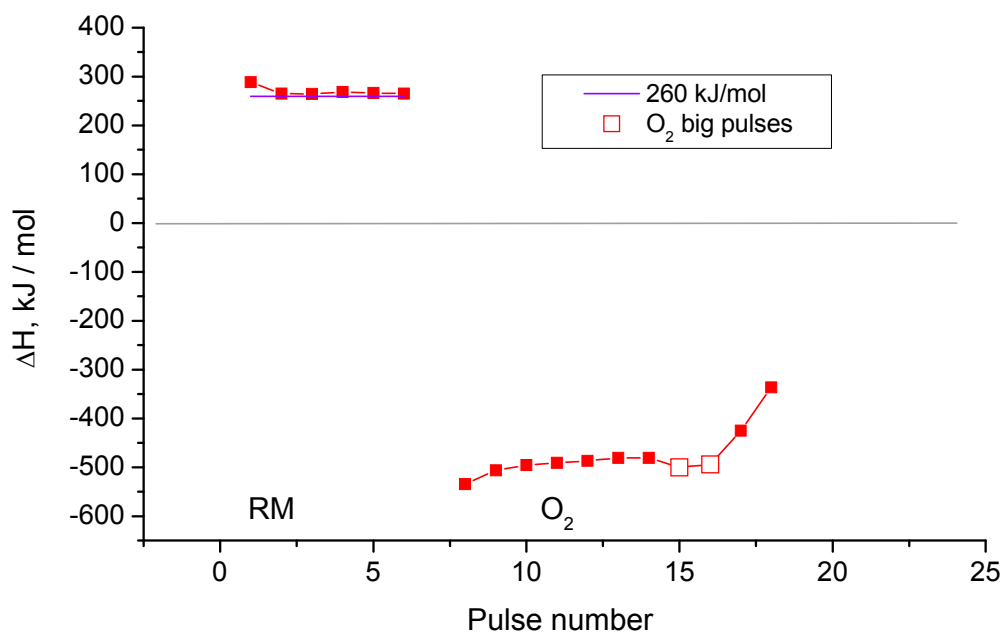


Figure 11. Measured heat effects for the series of the reaction mixture pulses followed by O₂ pulses at 773 K.

3. Materials and Methods

A continuous preparation technique in supercritical alcohol medium was employed for the preparation of Ni/ceria-zirconia catalysts with controllable particle size of the mixed oxide support and nickel dispersion [14]. The average particle sizes of ceria-zirconia and nickel oxide were estimated by the Selyakov-Scherrer equation from the integral broadening of the most intensive (002) and (200) XRD (X-ray diffraction) peaks, respectively. Transmission electron microscopy (TEM) micrographs were obtained with a JEM-2010 instrument (JEOL Ltd., Tokyo, Japan). The nickel (NiO) particle size was estimated by measuring the size of at least 150 particles. Rates and heats of the catalysts reduction/reoxidation by pulses of CH₄/CO₂/O₂ in He for catalysts after different pretreatment were estimated using a Setaram Sensys DSC TG calorimeter (Setaram Instrumentation, Caluire-et-Cuire, France) and a pulse kinetic installation equipped with gas chromatograph Chromos GH-1000 (Chromosib, Moscow, Russia), mass-spectrometer UGA-200 (Stanford Research Systems Inc., Sunnyvale, CA, USA), and gas sensors. The catalyst sample (0.033 g) was loaded in a quartz tube which was located in a measuring channel of the calorimetric unit. In the comparison channel an empty reactor was placed. Inlet gas feed was produced by the gas-mixing installation and pulses were introduced into the reactor by a six-port valve. The catalyst steady state was achieved using a continuous flow of the reaction feed followed by purging reactor with the He stream for 30 min and supplying several consecutive pulses of the reaction mixture at certain temperature, namely 773 and 973 K. The volume of each pulse was equal to 0.85 mL or 3.6 mL, the time interval between pulses 20 min. Further details are described elsewhere [13].

Conversion of reagents *X* was estimated as follows:

$$X_{CH_4} = \frac{C_{CH_4}}{C_{CH_4}^0 - C_{CH_4}}$$

$$X_{CO_2} = \frac{C_{CO_2}}{C_{CO_2}^0 - C_{CO_2}}$$

and selectivity *S* in the current work is defined as

$$S_{H_2} = \frac{C_{H_2}}{C_{CH_4}^0 - C_{CH_4}}$$

$$S_{CO} = \frac{C_{CO}}{C_{CH_4}^0 - C_{CH_4}}$$

$$S_{CO_2} = \frac{C_{CO_2}}{C_{CH_4}^0 - C_{CH_4}}$$

where C_i is concentration of certain component in products mixture, C_i^0 initial concentration, S_{CO_2} was calculated in the case of CH_4 pulses only.

The amount of oxygen removed from the catalyst by CH_4 pulse or inserted by CO_2/O_2 pulse was expressed either as a fraction of the total amount of oxygen in oxidized sample or a number of the oxygen monolayers (one monolayer is equal to 10^{19} atoms m^{-2}).

4. Conclusions

The studied process of methane dry reforming can be described by a sequential redox scheme and the activation of methane and carbon dioxide occurs independently. Oxidation of methane with release of the synthesis gas components is accompanied by a partial reduction of the catalyst, while reoxidation of the sample with carbon dioxide is a necessary stage for the replenishment of mobile oxygen. Calculated values of the heat of oxygen chemisorption during feeding pulses of CH_4 , CO_2 , or CO reliably agree with each other and amount to about 650 kJ per mol O_2 , which corresponds to bridging oxygen forms.

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Author Contributions: M.Y.S. prepared and characterized sample for studies; V.A.S. and V.A.R. planned and designed microcalorimetric experiments; V.A.R. and M.N.S. performed experiments and analyzed the data; M.N.S. and V.A.S. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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