

# Oscillations of partial oxidation of methane over H-ZSM-5 supported rhodium catalyst

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## Abstract

A Rh/H-ZSM-5 catalyst has been found to catalyse the partial oxidation of methane at atmospheric pressure, and regular oscillations in both reactants and products have been observed. Temperature-programmed techniques, such as TPD, TPO and TPR, were performed to look into the reaction mechanism. The oscillatory behavior may be attributed to the synergism of the formate species and the oxide with certain interaction with the support.

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**Keywords:** Methane partial oxidation; Oscillation; Rh/H-ZSM-5 catalyst; Synergism

## 1. Introduction

Revelation of regimes of oscillatory behavior in catalytic processes may lead to new insights into the reaction mechanisms and achieve a better understanding of the operation and improvement of the practical catalysts [1]. Studying this behavior can provide information which could not be extracted from the analysis in the nonoscillatory mode [2]. The oscillatory behavior during the catalytic oxidation/combustion of methane over the supported and unsupported nickel [3–8] and palladium [9–13] catalysts has been the subject of considerable number of recent publications. However, the oscillatory mechanism is still not understood in detail, although it is generally accepted that the cyclic oxidation/reduction process is responsible for the oscillation.

Ruckenstein and Hu [3] were the first who observed catalyst temperature oscillation during partial oxidation of methane over supported nickel catalyst. They considered that

the hot spots on the Ni/SiO<sub>2</sub> catalyst moving up and down caused the oscillation of the catalyst temperature, and were probably due to the reduction and oxidation of the catalyst by the reactants. But no oscillations were detected in the product concentrations. In a series of studies conducted by Zhang et al. [6–8,14] in the partial oxidation of methane (POM) reaction, the oscillations were observed in terms of reactant and product concentrations, as well as temperatures, and in general, maxima in the product oscillations of CO<sub>2</sub> and CO (H<sub>2</sub>) corresponded to minima in the CH<sub>4</sub> and O<sub>2</sub> reactant oscillations. The results obtained from the experiments indicated that methane oxidation was related to the behavior of the catalyst surface switching back and forth from the reduced state to the oxidized state.

In this paper, we report the first observation of oscillations over Rh/H-ZSM-5 catalyst with certain SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio when an argon/methane/oxygen mixture was passed, and the further investigations into the oscillatory reaction kinetics. The oscillations were studied in terms of reactant and product concentrations. By varying the reaction conditions, the regime of oscillatory behavior has been changed, which could lead to new insights into the oscillation mechanism.

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## 2. Experimental

### 2.1. Materials

The catalysts were prepared by impregnating H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$  and 50, nominated as H25 and H50, BET surface area 329 and 301  $\text{m}^2/\text{g}$ , Nankai University) with an aqueous solution of  $\text{Rh}(\text{NO}_3)_3$  in order to have a final Rh loading of 1 wt.%. The support H-ZSM-5 is precalcined in the muffle at 800 °C for 4 h. After impregnation, the samples were dried and then calcined at 800 °C for 4 h, giving the catalysts designated as fresh. The resultant catalysts for the test were crushed and sieved. Rh supported on  $\text{SiO}_2$  (BET surface area 230  $\text{m}^2/\text{g}$ , Aldrich) and  $\gamma\text{-Al}_2\text{O}_3$  (BET surface area 145  $\text{m}^2/\text{g}$ , Alfa) samples were prepared with the same method for comparison.

The structure and the composition of the catalysts were determined by the X-ray diffraction using Rigaku Dmax/RC instrument with the Cu  $K\alpha$  radiation at 40 kV and 30 mA. It was observed, from the X-ray diffraction patterns of the Rh/H-ZSM-5 catalysts obtained before and after reaction, that the samples submitted to the reaction conditions shows the lowest intensity of the high miller index diffraction peaks of the zeolite, meaning a partial destruction of the zeolite matrix. No Rh-based phases are detected by XRD due to low metal loading (1 wt.%).

### 2.2. Apparatus and procedure

The temperature-programmed tests were carried out in a fixed bed quartz reactor connected to a quadruple mass spectrometer (Baltzers QMS 2000) at atmospheric pressure. The amount of catalyst was 40 mg. The reactor was inserted into an oven, and the temperature was controlled by ÜGU-AI-708 controller. The temperature was measured by a K-type thermocouple. The reactant mixture, consisting of a pre-mixed gas ( $\text{CH}_4:\text{O}_2:\text{Ar} = 2:1:45$ ), was introduced in the reactor with a total flow rate of 10 ml/min in the TPSR (temperature-programmed surface reaction) experiment. The temperature increased at 15 K/min till the required point, and that is for all experiments.

The reduction of the catalysts were performed by heating the sample from RT to 800 °C in 5%  $\text{H}_2/\text{Ar}$  with the flowrate 10 ml/min. The reoxidation of the catalysts and identification of coke on the catalysts were measured by oxidation in 20%  $\text{O}_2/\text{He}$  (20 ml/min). TPD experiments were carried out in the pure helium flow (20 ml/min).

## 3. Results

### 3.1. Oscillatory behavior of the Rh/H50 catalyst in $\text{CH}_4\text{-O}_2\text{-Ar}$ mixtures and the influence of temperature

The occurrence of the oscillations during the POM reaction was observed by studying the catalytic behavior of the

fresh catalysts samples in their TPSR experiments, as shown in Fig. 1. It should be noted that the QMS signal of both the reactants and products illustrated in the figures have been vertically offset by the factors shown in the figures. Oscillations were observed for the Rh/H50 catalyst. The typical oscillation patterns displayed during the partial oxidation of methane for Rh/H50 at low and high temperatures are depicted in Fig. 2. The frequency was found to be dependent on the temperature. The increase in the frequency of the oscillation with rising temperature is due to the increase in the transformation rate of the chemical state of catalytic surface. Fig. 3 shows two complete oscillation cycles of Fig. 2c. It can be seen that CO and  $\text{H}_2$  oscillated with the minimum production corresponding to the  $\text{CO}_2$  peak in production. Maxima in the product oscillations of CO correspond to minima in the  $\text{CH}_4$  reactant oscillation, and there is an appreciable hysteresis in the peak of  $\text{H}_2$ . These phenomenon are quite different from Zhang's description in their articles. It can also be seen that the oxygen signal is always close to zero, showing that virtually all of the oxygen was used up in the reactions and oscillations. Thus, the rate of oxygen uptake remained constant, even though the production of oxygen containing products fluctuated wildly. This observation can only be explained if the oxygen was alternatively stored and then released from the surface. On this basis, the sharp peaks can be associated with the rapid reduction of rhodium oxide and the long tail that follows with the re-oxidation of the surface. That would be discussed in detail later.

### 3.2. The effects of catalyst pretreatment

To obtain information on the influence of catalyst pretreatment on the occurrence of oscillations, tests were made in which the catalyst was preheated using different feed compositions. The results of the activity in POM after the introduction of the reaction mixtures are shown in Fig. 4 for three different types of pretreatment to 800 °C: (i) in a feed of 20%  $\text{O}_2/\text{He}$ , (ii) in a feed of 5%  $\text{H}_2/\text{Ar}$ , and (iii) in a feed of pure helium.

In the case of the pretreatment in the oxidation gas mixture, the reaction exhibited more regular oscillatory behavior than that over the fresh catalyst (Fig. 4a). The TPSR profiles obtained for the Rh/H50 catalyst after preheated in the 5%  $\text{H}_2/\text{Ar}$ , as shown in Fig. 4b, the induction time before oscillations was shortened. In the case of pretreatment in helium only, the performance of the reaction was stable and high (Fig. 4c). This data clearly show that helium in the feed determines a complete change in the dynamic reactivity characteristics of the catalyst.

To obtain further information on the role of rhodium oxide species in changing catalyst reactivity, a different type of experiment was carried out. In these tests, the same pretreatment to 800 °C in the reduction and helium flow was made, but after the reactor was cooled to RT, the catalyst was further pretreated using 20%  $\text{O}_2/\text{He}$  heated up to 800 °C. Oscillations were not observed on the reduced/re-oxidation samples, as

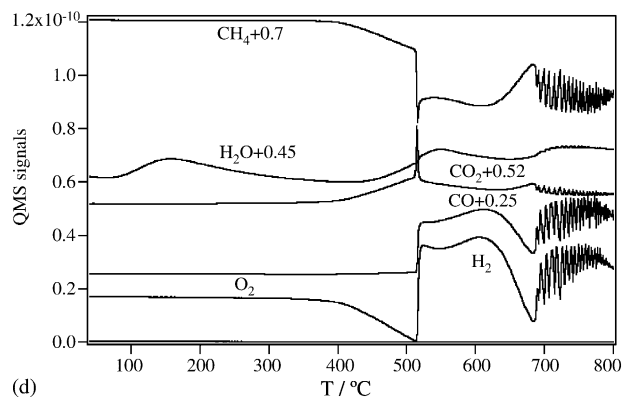
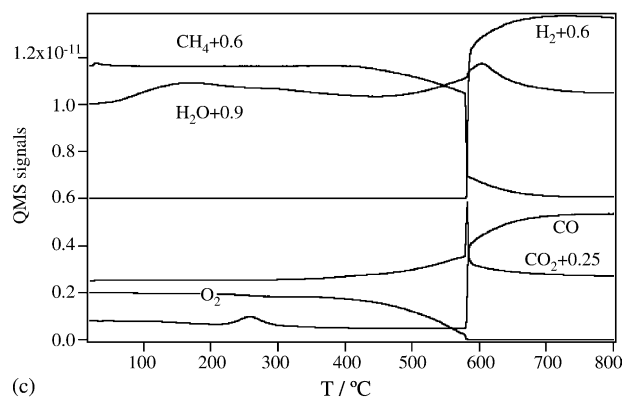
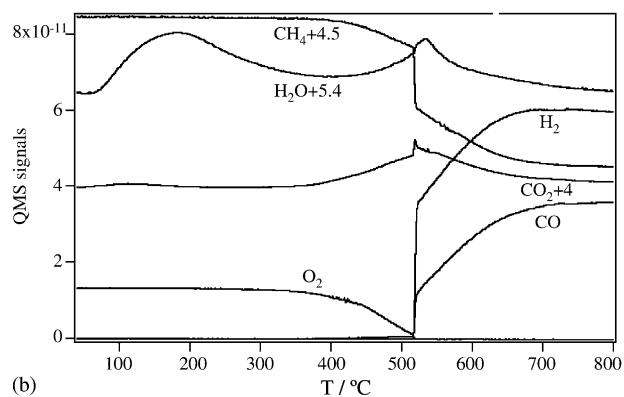
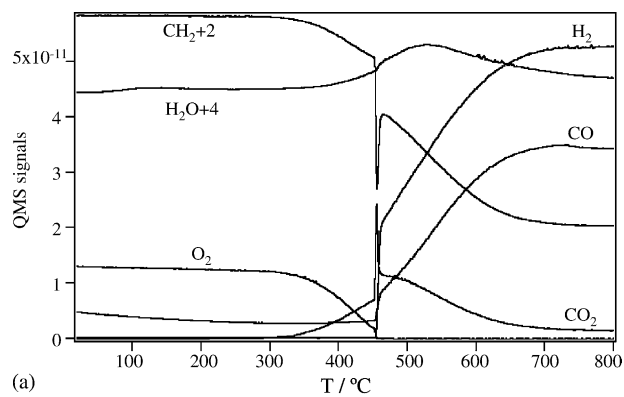


Fig. 1. The TPSR profiles for the rhodium catalysts with different supports: (a) SiO<sub>2</sub>, (b) γ-Al<sub>2</sub>O<sub>3</sub>, (c) H-ZSM-5, Si/Al<sub>2</sub> = 25, (d) H-ZSM-5, Si/Al<sub>2</sub> = 50.

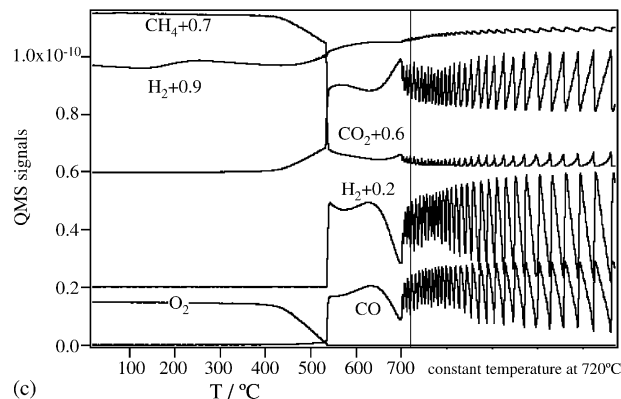
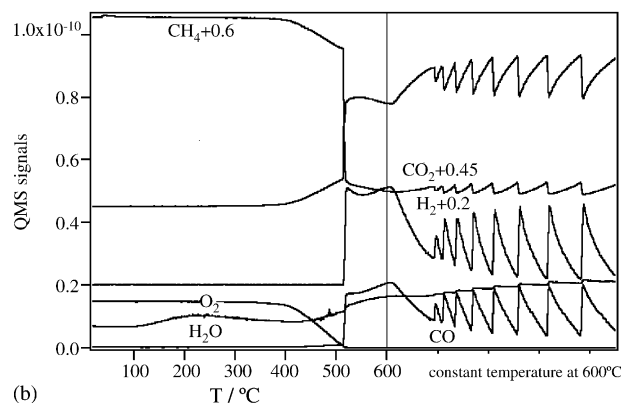
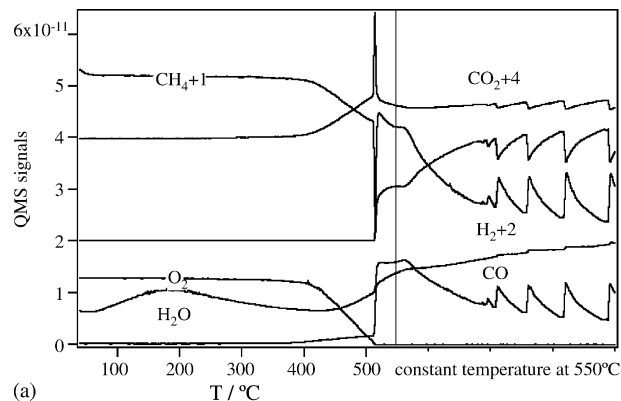


Fig. 2. The reaction behavior of the Rh/H50 catalyst at different temperatures: (a) 550 °C, (b) 600 °C, (c) 720 °C.

shown in Fig. 5a, but the data obtained give information that at high temperature, the catalyst was deactivated. In the case of the helium/re-oxidation catalyst, as shown in Fig. 5b, the performance of the reaction was still stably high.

### 3.3. Temperature-programmed reduction, desorption and oxidation studies

#### 3.3.1. TPD–TPR

To better understand how the helium pretreatment affects subsequent reaction, TPD experiment was carried out on all the fresh catalysts. As shown in Fig. 6, it can be observed that

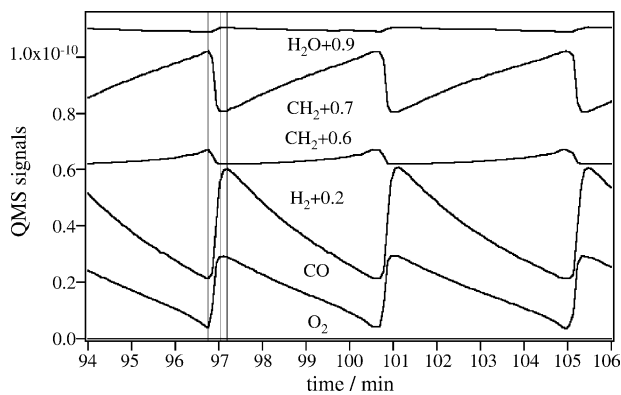
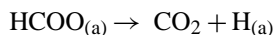


Fig. 3. Two complete oscillation cycles of Rh/H50 undergoing reaction at 720 °C.

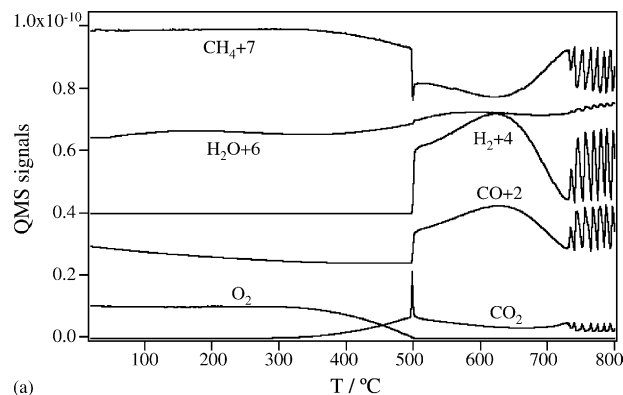
the Rh/SiO<sub>2</sub> catalyst had oxygen desorption peak, while the Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh/H-ZSM-5 catalysts had not.

In the following TPR experiments (Fig. 7), all the catalysts were tested under identical conditions. It can be observed that the Rh/SiO<sub>2</sub> sample exhibits a dominant reduction peak at 185 °C and smaller peak at 150 °C. The Rh/H50 catalyst has the reduction peak at about 185 °C, and the Rh/H25 catalyst was reduced at 210 °C. Comparing the TPR profiles before and after the TPD, no H<sub>2</sub> consumption peak is observed on the Rh/H50 sample pretreated in He which indicates complete autoreduction. Considering the Rh/H50 catalyst has no oxygen desorption peak, it can be supposed that during the TPD process, the rhodium oxide maybe react with the H<sub>(a)</sub> produced by the decomposition of surface formate species bound to the Si–O–Al groups [15],

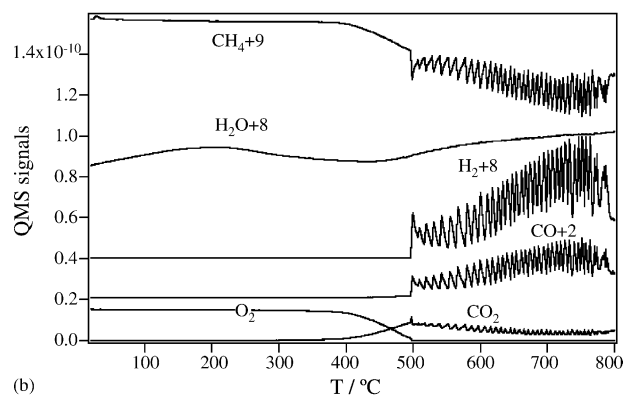


which is illuminated by the production of H<sub>2</sub> (Fig. 6B). Meanwhile, the Rh/H25 catalyst also has no oxygen desorption peak, but its reduction peak partly remains even after pretreatment in He flow; so it can be assumed that the rhodium oxide formed on the catalyst may have strong interaction with the support, and the formate formed on the catalyst cannot afford enough hydrogen to reduce all the rhodium oxides. Since the Rh/H25 catalyst has no oscillatory behavior, it appears that the rhodium oxide which strongly interacts with the support would not be favorable for the oscillations.

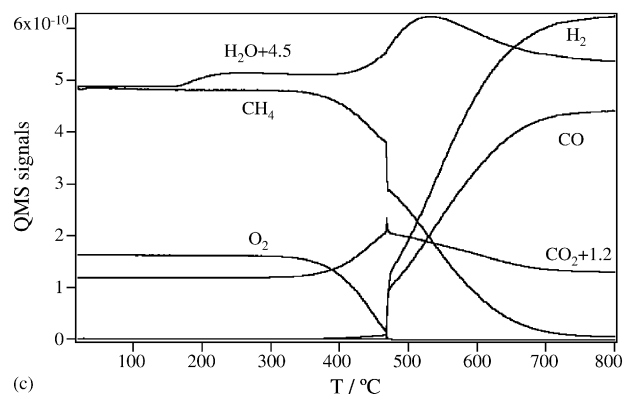
In order to determine if the rhodium-oxygen species can be resumed by reoxidation, the reduced Rh/H50 sample was oxidized to 800 °C. The results are shown in Fig. 8 and indicate that the high-temperature species (at 185 °C) shift to the low-temperature ones (at 150 °C) after a reduction–oxidation cycle. In view of the performance of this sample in the reaction (shown in Fig. 5a), it can be concluded that the rhodium oxides which can be reduced at lower temperature is not responsible for the oscillations. Moreover, when the fresh Rh/H50 catalyst was pretreated with 20% O<sub>2</sub>/He or with the followed by reoxidation, the high-temperature species remains, but the reaction performance of these two catalysts are quite different; the former has oscillations and the lat-



(a)



(b)



(c)

Fig. 4. The TPSR profiles for the Rh/H50 catalyst preheated in different gases: (a) in a feed of 20% O<sub>2</sub>/He flow, (b) in a feed of 5% H<sub>2</sub>/Ar, (c) in the pure helium flow.

ter is stable. These results indicate that the rhodium-oxygen species with the reduction peak at 185 °C is a key factor responsible for the oscillations, but not the only factor.

### 3.3.2. Identification of coke

The TPO profiles showing the CO<sub>2</sub>(*m/e* = 44) signals of the fresh rhodium catalyst on different supports are depicted in Fig. 9. The CO<sub>2</sub> desorption peak of the formate at about 360 °C can be observed over Rh/H-ZSM-5 catalysts. Meanwhile, it can be seen from the TPO profiles of the used catalysts (shown in Fig. 10) that the coke which should be eliminated only at high temperature was formed and accumu-

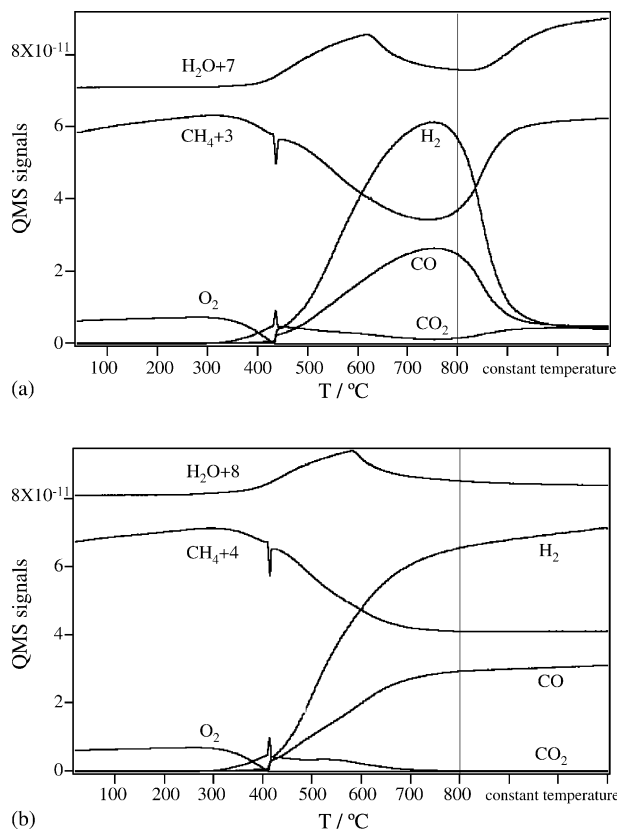


Fig. 5. The TPSR profiles for the Rh/H50 catalysts pretreated in 20% O<sub>2</sub>/He: (a) reduced Rh/H50 catalyst, (b) Rh/H50 catalyst heated in He to 800 °C.

lated during the reaction over the Rh/H-ZSM-5 catalysts. This is a supplementary proof indicating that the different characteristic of the rhodium-oxygen species on the Rh/H50 and Rh/H25 catalyst are responsible to the oscillation occurrence, since they have similar ability in the formation of carbonaceous species. In addition, the reduced Rh/H50 catalyst also have the CO<sub>2</sub> desorption peak at about 360 °C (shown in Fig. 11); so it is reasonable to think that the formate species would be involved in the oscillation mechanism. Moreover, compared to the fresh Rh/H50, the catalyst pretreated with the 20% O<sub>2</sub>/He flow exhibited more regular oscillatory behavior during the TPSR process (shown in Fig. 4a), indicating that the TPO process can eliminate only part of the formate. Only the catalyst pretreated in pure helium flow show no desorption peak (shown in Fig. 11) and perform stably because the formate could be eliminated completely after He treatment at high temperature. Even though the high-temperature oxygen species can be resumed by the reoxidation treatment (Fig. 8c), the absence of the formate restrain the oscillations.

As we know, the solid-state defects which are positive holes on oxygen atoms of zeolite framework generated by thermal activation under flow of oxygen or air have been claimed to be responsible for the remarkable oxidizing power of zeolites [16], and this power was also pointed out to be the center where the formate was formed [15]. For this reason, during the catalyst preparation, these positive holes could

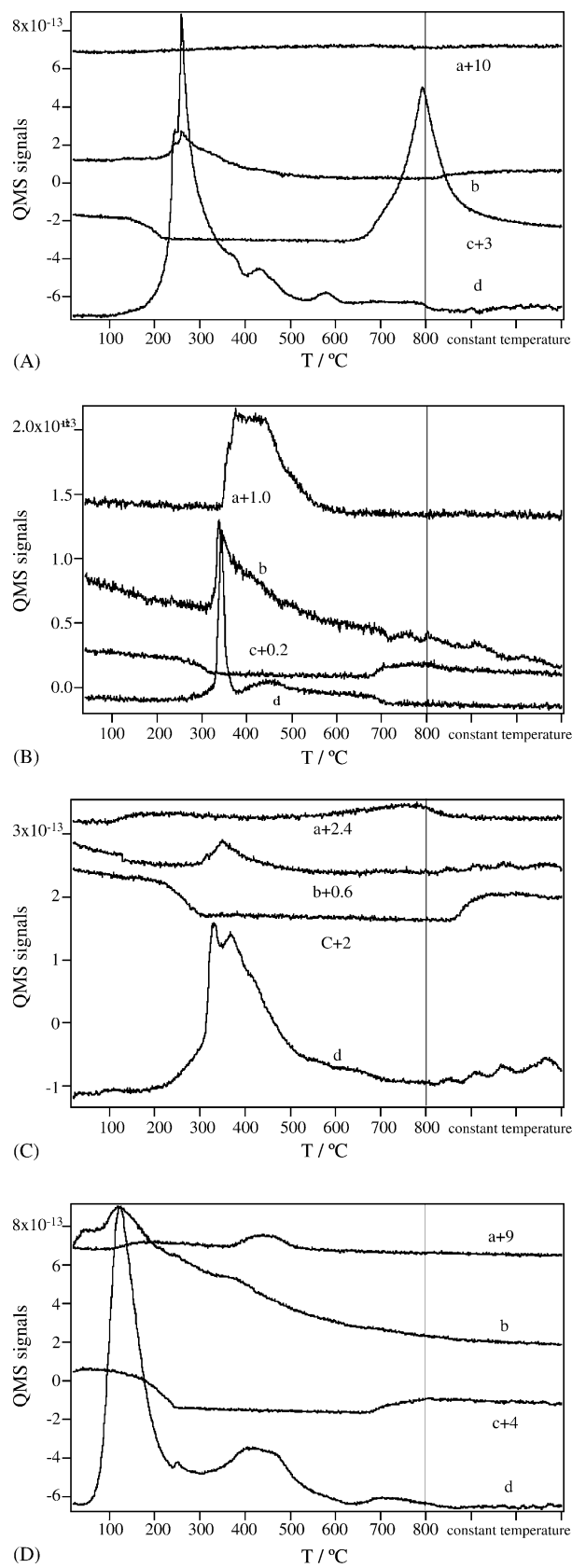
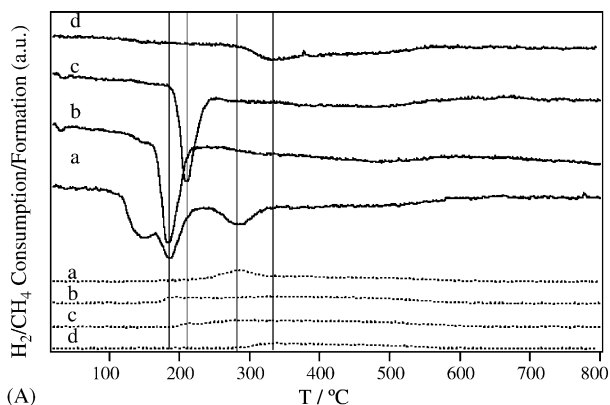
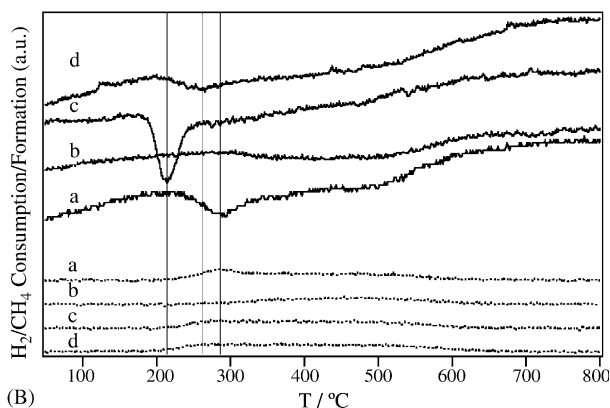


Fig. 6. The TPD profiles for the rhodium catalysts with different supports: (a)  $m/e = 2$ , (b)  $m/e = 28$ , (c)  $m/e = 32$ , (d)  $m/e = 44$ , (A) SiO<sub>2</sub>, (B) H-ZSM-5, Si/Al<sub>2</sub> = 50, (C) H-ZSM-5, Si/Al<sub>2</sub> = 25, (D)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.



(A)



(B)

Fig. 7. Profiles for H<sub>2</sub> uptake (solid line) and CH<sub>4</sub> evolution (dotted line) obtained in TPR of the fresh rhodium catalysts with different supports: (a) SiO<sub>2</sub>, (b) H-ZSM-5, Si/Al<sub>2</sub> = 50, (c) H-ZSM-5, Si/Al<sub>2</sub> = 25, (d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (A) fresh catalysts, (B) catalysts pretreated in He at 800 °C.

decide the position where the rhodium oxide formed, and they can also decide the deposition place of the formate which could be originated from CO<sub>2</sub> in air even at room temperature. As an example, when the Rh/H50 sample pretreated in the pure helium was exposed in air for days, it could be observed that there appeared CO<sub>2</sub> desorption peak at about 360 °C during the TPO process and performed in the reaction just like the reduced catalysts.

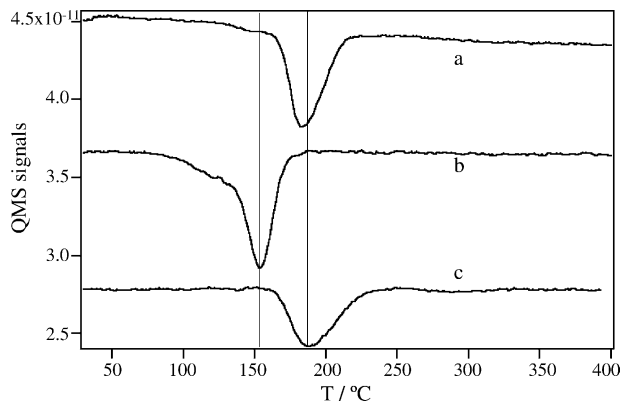


Fig. 8. The TPR profiles to 400 °C: (a) fresh Rh/H50 catalyst reoxidized to 800 °C, (b) reduced Rh/H50 catalyst reoxidized to 800 °C, (c) Rh/H50 catalyst pretreated with He flow followed by reoxidized to 800 °C.

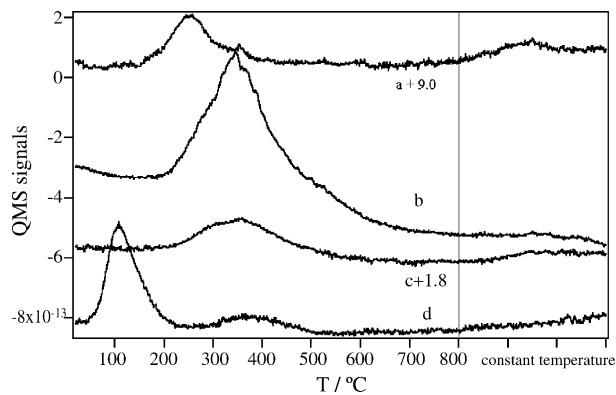


Fig. 9. CO<sub>2</sub> signals of the TPO profiles for the fresh rhodium catalysts with different supports: (a) SiO<sub>2</sub>, (b) H-ZSM-5, Si/Al<sub>2</sub> = 50, (c) H-ZSM-5, Si/Al<sub>2</sub> = 25, (d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

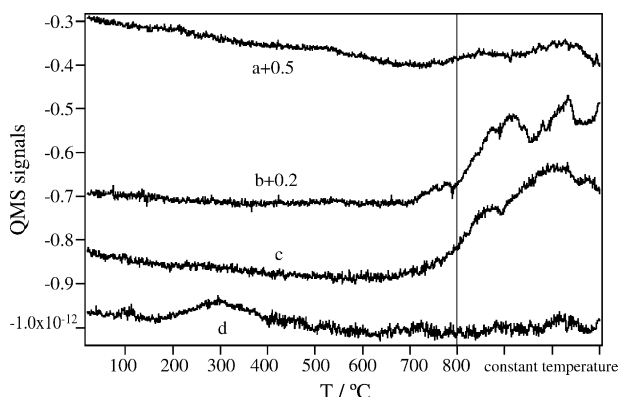


Fig. 10. CO<sub>2</sub> signals of the TPO profiles for the used rhodium catalysts with different supports: (a) SiO<sub>2</sub>, (b) H-ZSM-5, Si/Al<sub>2</sub> = 50, (c) H-ZSM-5, Si/Al<sub>2</sub> = 25, (d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

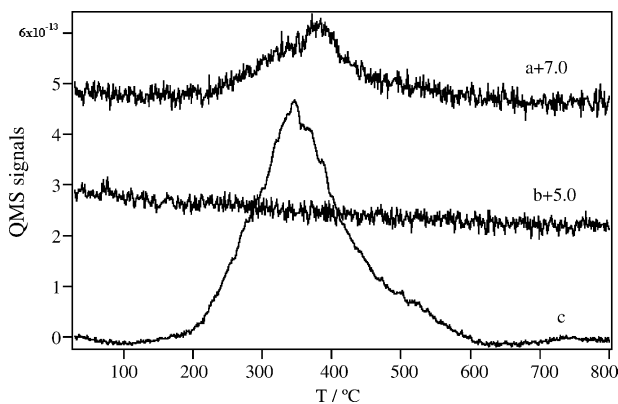


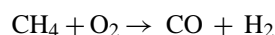
Fig. 11. CO<sub>2</sub> signals of the TPO profiles to 800 °C: (a) reduced Rh/H50 catalyst, (b) Rh/H50 catalyst pretreated by the He flow, (c) fresh Rh/H50 catalyst.

#### 4. Discussion

It is now accepted that oscillations in reactions over supported metal catalysts are caused by surface transformations occurring at the crystallite level [1], such as periodical oxidation and reduction of the catalytic surface [17,18], or

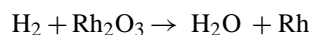
transitions between different surface phases [19,20] rather than from impurities in the feed gas. With feed-gas compositions close to the stoichiometric value and at a sufficiently high temperature, the reactant gases may modulate the catalytic surface by influencing the  $\text{RhO}_x/\text{Rh}$  ratio in the active phase. Since the fresh Rh/H50 catalyst was pretreated by air at the reaction temperature until a relatively stable state was achieved, the supported metal catalyst was in the predominantly oxidized state before it was exposed to the reaction mixture. The observed induction period before oscillations commenced, and the further time required for stable oscillations to be established, tend to support this explanation. The catalyst surface would have been modulated gradually from being oxidized into a state in which the phases of metal oxides and metal coexisted, with corresponding fluctuations in activity.

According to the oxidation/reduction mechanism, at the low conversion state of oscillations, the high concentration of  $\text{CO}_2$  favor the formation of rhodium oxides. The presence of water may produce surface hydroxyl groups via dissociation of water that leads to a decomposition of the initially formed formate species at the metal–support interface, and these regenerated active sites play a role for accelerating of the  $\text{CO}_2$  dissociation by rising  $\text{CO}_2$  concentration in the vicinity of Rh particles by trapping  $\text{CO}_2$  as formate, which produce CO after its decomposition. CO adsorbs and accumulates on the oxidized Rh surface during this low conversion state. When the CO coverage reaches a critical value, reduction of Rh becomes fast and the POM reaction rate increases.



With increasing temperature, less CO accumulation is required for the onset of oxide reduction. This can be employed to explain the observed decrease in the period of the oscillations as the reaction temperature increases.

It can also be expected that hydrogen was used to accelerate the reduction of the rhodium oxide,



so a more reduced working state of the catalyst surface was to be stabilized, where there would be more hydrogen produced, so the strongly positive feedback occurred.

In the presence of large amount of CO, the surface formate species resulted from the interaction of CO with OH group on the zeolite assisted by the presence of gas phase  $\text{O}_2$  and were stable, so they inhibit the  $\text{CO}_2$  adsorption and subsequent hydrogenation of the adsorbed  $\text{CO}_2$ . The  $\text{CO}_2$  signal began to rise up at the point of the  $\text{H}_2$  signal attenuation, indicating that re-oxidation was beginning to occur. This final stage of the oscillation appeared to correspond to the reaction occurring over the metal on a decreasing amount of surface as the oxide layer progressively builds up. This leads to a decrease of Rh activity of partial oxidation of methane but favor to the formation of  $\text{CO}_2$  and reached to the top at the point of the beginning of the new oscillation cycle.

This reasoning can also explain the oscillating behavior observed on other pretreated Rh/H50 catalysts. The increasing magnitude of the oscillations on the reduced catalyst can be interpreted if the redox cycle, which was believed to be responsible for the oscillations, began on a small part of the surface and then slowly extended to cover the whole surface. Moreover, the induction period before oscillations was shortened because of the more reduced state of the rhodium species of the reduced sample than that on the fresh catalyst.

The oxidation pretreatment in the 20%  $\text{O}_2/\text{He}$  did not change the state of the rhodium oxide, but eliminate part of the formate on the fresh catalyst. So the more regular oscillatory behavior of this catalyst than that on the fresh sample was probably due to the decreased amount of the initially formed formate species on the catalyst. Therefore, it is understandable that when the fresh catalyst was pretreated in the helium only, the formate decomposed completely and the subsequent reaction is stable.

In the case of the pretreatment of the reduced Rh/H50 catalyst in 20%  $\text{O}_2/\text{He}$ , the high-temperature oxygen species shift to the low-temperature ones, indicating that the interaction between the metal and the support was weakened because of the assemble of the metal particles during the reoxidation process. So the active site on the support that were effective for  $\text{CO}_2$  activation decreased, and at high temperature, the formate species which are far from the Rh particles and cannot decompose under reaction condition maybe transformed into more stable “coke” which would be responsible for catalyst deactivation by blocking the pores and/or pore intersections inside the zeolite.

As compared with the Rh/H50 catalyst, the Rh/H25 has more protons acted as chemical anchors for the metal particles in zeolite cages and stabilize the high metal dispersion, so there are more active sites for  $\text{CO}_2$  activation, and the initially formed formate could be mainly adjacent to the metal–support interface, which can decompose efficiently under reaction condition. As for the Rh/H50 catalyst, because of the lower aluminum content, local Si–Al sequences described as “Al pairs”  $[\text{Al}-\text{O}-(\text{Si}-\text{O})_{1-2}-\text{Al}]$  and “single” Al atoms  $[\text{Al}-\text{O}-(\text{Si}-\text{O})_{\geq 3}-\text{Al}]$  are more far apart in its frameworks. So the initially formed formate species cannot decompose efficiently during the reaction, and that would cause deactivation, partly participating in oscillations.

In summary, the oscillatory behavior of the Rh/H50 catalyst is due to the synergism of the formate and the rhodium oxide with certain interaction with support. The different dispersion state of the rhodium species and the formate on the Rh/H-ZSM-5 catalyst is probably due to the Al distribution in ZSM-5 zeolite and the surface restructuring during the pretreatment. Further research is required to follow the oscillations in terms of reactant and product concentrations, as well as temperatures and gathering more information using a variety of surface science techniques before the detailed mechanism of this reaction can be elucidated.

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