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Effects of calcination temperatures on the catalytic performance of Rh/Al_2O_3 for methane partial oxidation to synthesis gas

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Abstract

Comparative studies using high temperature *in situ* Raman spectroscopy, TPSR, pulsed reactions of CH_4, H_2-TPR and O_2-TPD techniques were carried out on Rh/Al_2O_3 calcined at 600 and 900 °C to elucidate the effect of calcination temperatures on the nature of the Rh species in the catalysts and its relationship with the catalytic performance of Rh/Al_2O_3 for partial oxidation of methane (POM) to synthesis gas. The results indicate that significant difference in the POM performance of Rh/Al_2O_3 catalysts calcined at 600 and 900 °C can be attributed to the formation of rhodium species of different nature after the samples were calcined in the air at above temperatures. Calcining a Rh/Al_2O_3 sample in the air at 900 °C caused not only the formation of more than 81% of rhodium species irreducible by H_2 at the temperature below 600 °C, but also affected the redox property of the RhOx species reducible at the temperature below 250 °C. Compared to the rhodium species in the Rh/Al_2O_3 calcined at 600 °C, those in the catalyst calcined at 900 °C possesses stronger Rh–O bonds and higher oxygen affinity. These factors would affect the concentration of oxygen species on the two catalysts under the POM reaction conditions and consequently affect the primary products of the reaction. The results of TPSR and *in situ* Raman characterizations on the POM reaction over the catalysts indicate that, Rh/Al_2O_3 in fully oxidized form are mainly responsible for complete oxidation CH_4 to CO_2 and H_2O. The catalysts abruptly changed its oxidation state at the temperature when POM reaction starts. The results of high temperature Raman characterizations also suggest that a rhodium species in which Rh may substitute for the Al site of Al_2O_3 was formed in the Rh/Al_2O_3 sample calcined in air at 900 °C. This rhodium species is difficult to be reduced to Rh metal by H_2 at temperature below 600 °C.

Keywords: Methane partial oxidation; Synthesis gas; Rh/Al_2O_3; Calcination temperature; Reaction mechanism; *In situ* Raman

1. Introduction

The partial oxidation of methane (POM) to produce CO and H_2 has received increasing attention in recent years, mainly because of its potential application as a commercial source of synthesis gas [1–4]. The elucidation of reaction pathways in POM to synthesis gas over supported transition metal catalysts is an important pre-requisite toward improved catalyst designs. It is also one of the basic step and the major challenge in the study of the POM reaction [5]. Two major questions regarding the reaction mechanism are (1) whether CO or CO_2 is the primary product, and (2) how does the chemical state of the catalyst change during the reaction [5]. Although numerous attempts have been made to understand the reaction mechanism of synthesis gas formation, the reaction pathway is still being debated. It was found that the reaction mechanism may depend on the chemical state of the catalyst surface as well as on the type and amount of oxygen species available [6–17]. It was also reported that catalyst supports may play a significant role in affecting activity, selectivity and stability of catalysts as well as the reaction mechanism in POM to synthesis gas [11,13,18–32]. Indeed, in some cases the effect of supports could be related to an interaction between metal and supports that eventually would affect the reducibility of the metal species [24,25,27,28].

Al_2O_3 supported Rh catalyst exhibits high stability with excellent activity and selectivity for the reaction and has been

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extensively studied [11,13,14,32–36]. It is well known that heating a Rh/Al_2O_3 sample in an oxidizing environment at temperature above 600 °C causes not only the oxidation of supported Rh particles, but also the formation of an oxidized form of rhodium which is difficult to be reduced to metal by H_2 at the temperature below 600 °C [37–39]. Since POM is an exothermic reaction, the temperature of catalyst particles during the reaction, especially those near the catalyst bed inlet, can be much higher than the furnace temperature [40]. Therefore studies on the effect of high temperature treatments on the catalytic performance of catalyst are an important step toward its application. Moreover, the nature of Rh species on Al_2O_3 upon high temperature calcination in an oxidizing environment is still being debated at this stage [37–39,41–47]. The previous results of *in situ* time-resolved FTIR spectroscopic characterization from our group suggest that the POM reaction over Rh/Al_2O_3 catalysts calcined at 600 and 900 °C, respectively, may proceed by distinctly different mechanisms; this suggestion is necessary since by the former catalyst CO is the primary product, while by the latter one (calcined at 900 °C) CO_2 is formed ahead of CO [48].

In this work, comparative studies using techniques of high temperature *in situ* Raman spectroscopy, temperature-programmed surface reactions (TPSR), pulsed reactions of CH_4, H_2-temperature-programmed reduction (TPR), and O_2-temperature-programmed desorption (TPD) were carried out over the Rh/Al_2O_3 catalysts calcined at 600 and 900 °C. It is expected that such experiments should provide with some useful information to understand the effects of calcinations temperatures on the nature of the rhodium species over Al_2O_3 and its relationship with the catalytic performance of the catalysts for POM to synthesis gas.

2. Experimental

2.1. Catalyst preparations

Rh/Al_2O_3 catalysts were prepared by the wet impregnation method using $RhCl_3\cdot nH_2O$ as the precursor for the metal. The Al_2O_3 support was calcined at 400 °C for 4 h before uses. After noble metal impregnation, the catalyst was dried at 110 °C and calcined at either 600 or 900 °C (denoted as Rh/Al_2O_3-600 and Rh/Al_2O_3-900, respectively) in the air for 4 h. The fresh catalysts were then reduced with H_2 at 600 °C for 30 min before subjecting to tests.

Most of the catalysts used in the study were prepared using the Al_2O_3 from China Medicine (Group) Shanghai Chemical Reagent Corporation (209 m^2/g). The catalysts used in the *in situ* Raman characterization and TPSR experiments were prepared using the Al_2O_3 from Guizhou Alumina Factory, China (TL-02, ~190 m^2/g), on the basis of its low Raman scattering background. The results of XRD characterization indicated that both supports were γ-Al_2O_3 [49].

2.2. The performance of catalysts

The catalytic performance for POM to synthesis gas was studied using $CH_4/O_2/Ar = 2/1/45$ mixture (in the volume ratio) as a reaction feed. The reaction was carried out in a fixed bed quartz tube reactor (5 mm i.d.) at the atmospheric pressure. The catalyst (15.0 mg) was reduced at 600 °C for 30 min before it was switched to take the reaction feed. The products were analyzed by an on-line GC equipped with TCD detector using Ar (99.999%) as the carrier gas and a carbon sieve column (1.5 m) for the separation of CH_4, O_2, H_2, CO and CO_2.

The TPSR experiments were performed by a Micromeritics AutoChem II 2920 instrument using $CH_4/O_2/He = 2/1/45$ mixture (in the volume ratio) as reactant. The catalyst (30.0 mg) was first reduced in a flow of $H_2/Ar = 1/9$ mixture (in the volume ratio, 50 mL/min) at 600 °C for 30 min and cooled down to 20 °C under the same atmosphere. The reduced sample was then purged with a flow of $CH_4/O_2/He$ mixture (50 mL/min) at 20 °C until the base line of the instrument was flat and heated from 20 to 800 °C at a rate of 10 °C/min. The products of the TPSR reaction were analyzed by an on-line ThermoStar quadrupole mass spectrometer (GSD301T2).

The pulsed reaction of CH_4 was carried out at 600 °C in a fixed bed quartz tube reactor with 50.0 mg catalyst using He containing a trace amount of O_2 as carrier gas. After reducing with H_2 at 600 °C for 30 min, the catalyst was purged with the carrier gas at the same temperature until the base line of the mass spectrometer was flat. The CH_4 pulses (99.9%, ~80 μL, at rt) were then admitted to the reactor every 6 min and the reaction products were analyzed by an on-line Balzers OmniStar quadrupole mass spectrometer (QMS 200).

2.3. Catalyst characterization

X-ray powder diffraction (XRD) analysis was carried out by a Panalytical X'pert PRO diffractometer scanning 2θ from 10° to 70°. Cu Kα radiation operated at 40 kV and 30 mA was used as the X-ray source.

The BET surface area of the catalyst was measured by N_2 adsorption at −196 °C using a Micromeretics Tristar 3000 instrument. Before the measurement, the samples were degassed at 300 °C for 2 h. The dispersion of the metal was determined by CO chemisorption at room temperature by assuming a 1/1 stoichiometry. The experiments were performed by a Micromeretics ASAP 2010 instrument. The catalyst sample (~1 g) was first reduced with H_2 (99.999%) at 600 °C for 30 min followed by evacuation at 360 °C for 30 min. The sample was then cooled down to 35 °C under vacuum for CO adsorption.

The H_2-TPR and O_2-TPD experiments were performed by a Micromeritics AutoChem II 2920 instrument. Prior to the TPR experiment, the catalyst (~0.4 g) was oxidized with $O_2/He = 1/4$ mixture (in the volume ratio, 20 mL/min) at 500 °C for 30 min and cooled down to 20 °C under same atmosphere. The sample was then purged with $H_2/Ar = 1/9$ mixture at 20 °C until the base line of the instrument was flat. The TPR profile of the catalyst was obtained by heating the above treated sample from 20 to 800 °C at a rate of 10 °C/min in a flow (50 mL/min) of $H_2/Ar = 1/9$ mixture. The hydrogen consumption was monitored by a TCD detector. The catalyst (~0.2 g) for the O_2-TPD experiment was also oxidized with $O_2/He = 1/4$ at 500 °C for 30 min and cooled down to 20 °C under same atmosphere. The

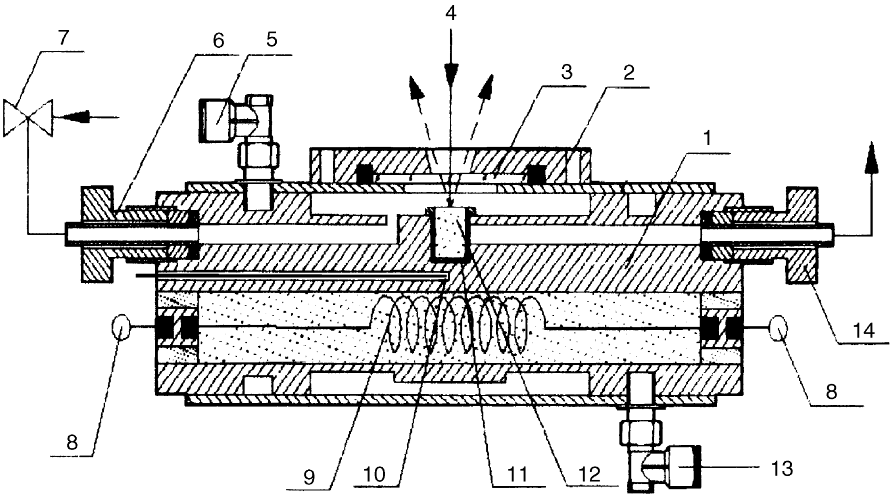

Fig. 1. Schematic diagram of the high temperature *in situ* Raman cell for Raman microscope. (1) Stainless steel cell body, (2) window holder, (3) quartz window, (4) laser beam, (5) cooling water outlet, (6) gas inlet, (7) flow adjusting valve, (8) heating wire connectors, (9) heating wire, (10) thermal couple, (11) sample holder, (12) sample, (13) cooling water inlet, (14) gas outlet.

sample was then purged with He (99.999%) at 20 °C for 30 min and heated from 20 to 1100 °C at a rate of 10 °C/min in a flow (50 mL/min) He. The O_2 desorption was analyzed by an on-line ThermoStar quadrupole mass spectrometer (GSD301T2).

In situ Raman experiments were performed with a Renishaw R1000 microprobe Raman system equipped with CCD detectors using a home built high temperature *in situ* Raman cell (Fig. 1). The microscope attachment for the spectrometer is based on a Leica DMLM system using an OFR LMU-15×-NUV objective. Powdered samples were pressed into the sample holder equipped with a thermocouple placed underneath for temperature measurement. The excitation wavelength was 325 nm with a power of ~3 mW measured at the analysis spot.

3. Results and discussion

3.1. Bulk structure, surface area and metal dispersion of the catalysts

Results of XRD characterization of the Rh/Al_2O_3 catalysts calcined at 600 and 900 °C show only the diffraction patterns of Al_2O_3 calcined at same temperatures. No diffraction line referring to the rhodium oxide or metallic Rh species was detected in the fresh or the reduced samples.

The BET surface area and metal dispersion of catalysts are listed in Table 1. The surface area of 1 wt.%Rh/Al_2O_3 is very close to that of the Al_2O_3 support calcined at same temperature. The metal dispersion datum for 1 wt.%Rh/Al_2O_3-600 is slightly over 1, which may have resulted from the adsorption of CO in the *gem*-dicarbonyl form [50–53]. Compared to the 1 wt.%Rh/Al_2O_3-600 catalyst, the measured CO/Rh ratio over 1 wt.%Rh/Al_2O_3-900 is very low. This is due to most of the oxidized rhodium species in the sample was unable to reduce to metal by H_2 at 600 °C (see H_2-TPR results shown below).

Table 1
BET surface area and metal dispersion of the samples calcined at 600 and 900 °C

Sample	Calcination temperature (°C)	BET surface area ($m^2\ g^{-1}$)	Reduction temperature (°C)	CO/Rh
Al_2O_3	600	209	–	–
Al_2O_3	900	121	–	–
1 wt.%Rh/Al_2O_3	600	205	600	1.06
1 wt.%Rh/Al_2O_3	900	124	600	0.04

3.2. Catalytic performance tests

3.2.1. Continuous flow reaction tests

The reaction was carried out at 600 °C (furnace temperature) and at a space velocity (SV) from 1.0×10^5 to 4.0×10^5 mL g cat^{-1} h^{-1}. The results are shown in Table 2. For the reaction over 1 wt.%Rh/Al_2O_3-600 catalysts, as the SV increased from 1.0×10^5 to 4.0×10^5 mL g cat^{-1} h^{-1}, the conversion of methane decreased, while the selectivity to CO was almost unchanged. For the reaction over 1 wt.%Rh/Al_2O_3-900 catalysts, however, both the conversion of methane and the selectivity of CO decreased with increasing SV. According to the direct partial oxidation mechanism [3,4], CO is the primary product of the oxidation of surface CHx ($x = 0$–3) species. An increase in SV should not result in the decrease of CO selectivity. On the other hand, if the reaction follows the combustion-reforming scheme [1], the first step of the reaction is the combustion of CH_4 to CO_2 and H_2O. CO is formed through the subsequent reforming reaction of unreacted CH_4 with either CO_2 or H_2O. Its selectivity will therefore decrease with an increasing SV. The effects of SV on the CO selectivity of the Rh/Al_2O_3 catalysts calcined at 600 and 900 °C suggest that the CO formation over the two catalysts might follow different pathways.

Although the reactant mixture (at $CH_4/O_2 = 2$) used in the experiment has been diluted with large amount of Ar, a hot spot layer still exists in the catalyst bed since the obtained CH_4 conversions on both catalysts are higher than the

Table 2
Effects of space velocity on the catalytic performance of 1 wt.% Rh/Al_2O_3 catalysts for POM to synthesis gas

Catalyst	Space velocity $\times 10^{-4}$ (mL g cat.$^{-1}$ h^{-1})	CH_4 conversion (%)	CO selectivity (%)	H_2 selectivity (%)
1 wt.%Rh/Al_2O_3-600	10.0	87.1	91.1	87.0
	20.0	86.6	90.6	85.7
	30.1	86.2	90.4	87.7
	40.0	84.9	90.6	84.9
1 wt.%Rh/Al_2O_3-900	10.1	68.0	77.9	76.5
	15.0	60.2	72.9	76.4
	29.5	52.8	68.4	67.8
	40.0	51.9	66.9	64.0

Feed: $CH_4/O_2/Ar = 2/1/45$; catalyst: 15.0 mg; furnace temperature: 600 °C; data were collected after 30 min on stream.

thermodynamic equilibrium value at 600 °C (CH_4 conversion = 55.0%) [40]. However, according to the CH_4 conversion data shown in Table 2, it can be estimated that the hot spot temperature on 1 wt.%Rh/Al_2O_3-600 is less than 800 °C (CH_4 conversion = 91.8%), and that on 1 wt.%Rh/Al_2O_3-900 is less than 700 °C (CH_4 conversion = 78.2%).

3.2.2. *TPSR characterization*

Fig. 2 shows the results of TPSR experiments over the 1 wt.%Rh/Al_2O_3 catalyst. The MS signals of the reactants and the products have been vertically offset by the factors shown in the figure. The reaction over 1 wt.%Rh/Al_2O_3-600 catalysts started at about 320 °C. When the temperature is below 516 °C, CO_2 and H_2O are the main products. Small amount of CO can also be detected above 400 °C. When the furnace temperature was increased to 516 °C, a sudden increase in the CO and H_2 MS signals was observed indicating that partial oxidation of CH_4 to synthesis gas ignited at this temperature, and the signal of O_2 decreased to zero at the same time. As the furnace temperature increasing from 516 to 800 °C, the amount of CO and H_2 increased smoothly, while that of CO_2 and CH_4 gradually decreased. On the 1 wt.%Rh/Al_2O_3-900 catalyst, the ignition temperature for POM is about 60 °C higher than that of 1 wt.%Rh/Al_2O_3-600, and oscillations in CH_4 and products (CO, H_2, CO_2 and H_2O) were observed when the furnace temperature was above 615 °C. The frequency of the oscillations was found to increase with the increasing of temperature. Similar

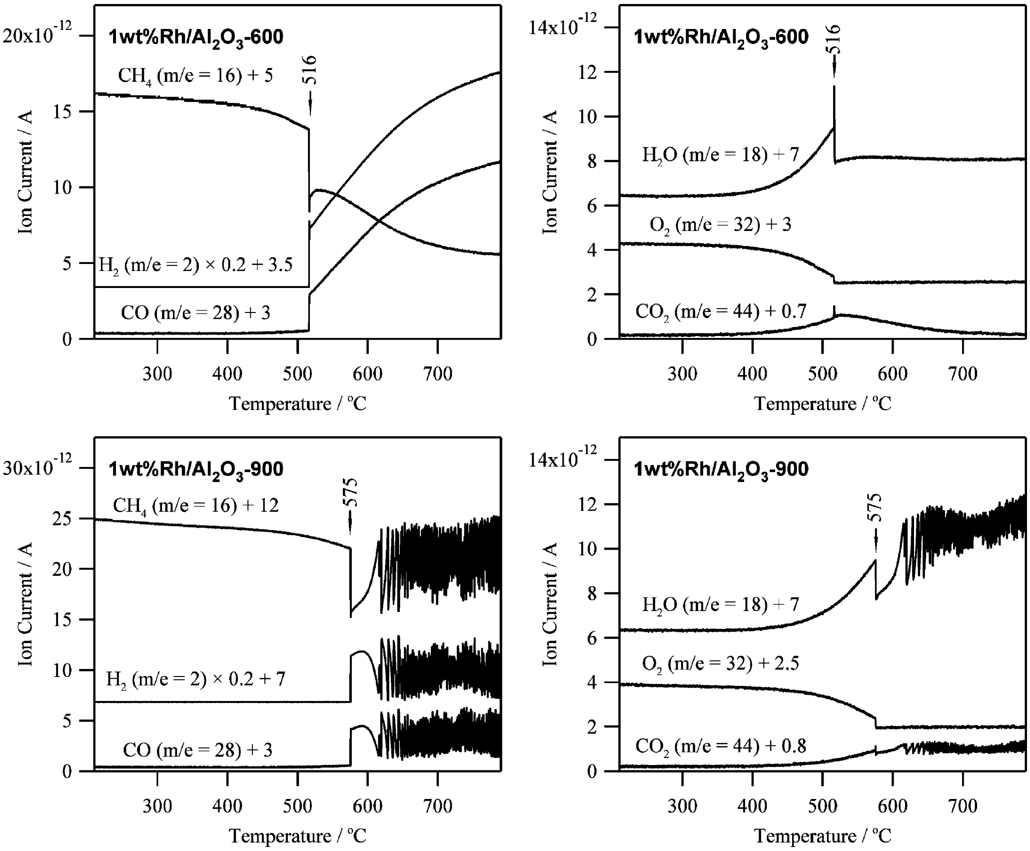

Fig. 2. TPSR profiles for the reaction of $CH_4/O_2/He = 2/1/45$ over the 1 wt.%Rh/Al_2O_3 calcined at 600 and 900 °C.

oscillatory behavior has been found during the POM reaction over the Ni, Co and Pd wires and foils [54–57], as well as over the H-ZSM-5 supported Rh catalyst [58]. According to the results of Zhang et al., the oscillation can be related to the behavior of the catalyst surface switching cyclically from the reduced state to the oxidized state during the reaction [54–57]. This suggests that the redox property of the rhodium species in the Rh/Al_2O_3 calcined at 900 °C is very different from those in the catalyst calcined at 600 °C. To prove this suggestion, a comparative study using the pulsed reaction of CH_4 was carried out over the two catalysts.

3.2.3. Pulsed reactions of CH_4

The results of pulsed reactions of pure CH_4 over the 1 wt.%Rh/Al_2O_3-600 and 1 wt.%Rh/Al_2O_3-900 catalysts are shown in Fig. 3. When pulses of CH_4 were introduced to the pre-reduced Rh/Al_2O_3-900 at the time interval of 6 min, the completely oxidized product, CO_2, was formed at every pulse. In contrast, CO_2 was only formed at the first three pulses (and never thereafter) when CH_4 was pulsed over Rh/Al_2O_3-600. These results are similar to those observed in the comparative studies of pulsed reactions of CH_4 over pre-reduced Rh/SiO_2 and Ru/SiO_2 catalysts [17], indicating that the metallic rhodium species in Rh/Al_2O_3-900 is easier to be oxidized than that in Rh/Al_2O_3-600. Based on the TAP study of the reaction over Rh/α-Al_2O_3 and Rh sponge, Hofstad et al. came to the conclusion that the primary products of CH_4 oxidation were dependent on the amount of surface oxygen species available [11]. The results of *in situ* time-resolved FTIR and microprobe Raman spectroscopic characterizations also suggested that surface O^{2-} is probably the main oxygen species on the Rh/SiO_2 and Ru/SiO_2 catalysts under POM condition, and is responsible for both the selective and complete oxidation of methane depending on its concentration on the catalyst surface [15–17]. In the above experiments, the amount of CH_4 introduced in each pulse was about 80 μL. If we suggest that all the rhodium species in the catalyst is reducible, it can be calculated that three pulses of CH_4 will be sufficient to reduce all the Rh_2O_3 species in the catalyst to the metallic state. Therefore, the source of the oxygen species in the catalysts responsible for the conversion of CH_4 to carbon oxides from the forth pulse onwards should mainly be O_2 in the He flow. Due to a difference in the oxygen affinity of the rhodium species in the catalysts calcined at 600 and 900 °C, metallic rhodium species in Rh/Al_2O_3-900 will be more easily oxidized by O_2 in the carrier gas than that in Rh/Al_2O_3-600. As a result, the amount of oxygen species accumulated on the Rh/Al_2O_3-900 surface between two pulses (6 min) will be great enough to oxidize CH_4 to both CO_2 and CO, while the oxygen species on Rh/Al_2O_3-600 favors the formation of CO only because its concentration on the catalyst surface is too low to completely oxidize CH_4 to CO_2.

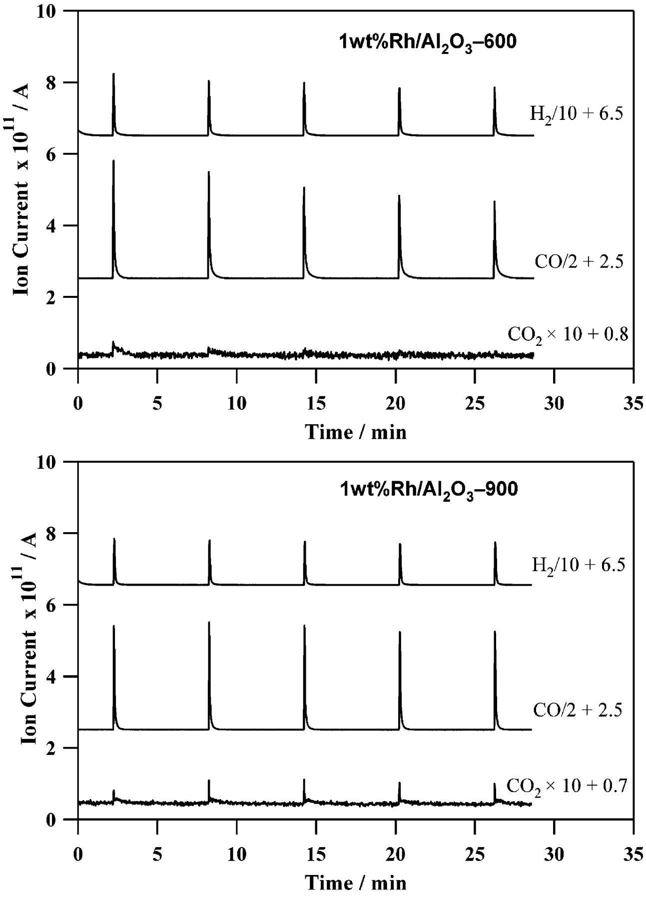

Fig. 3. CO and CO_2 formations by pulsing CH_4 over 1 wt.%Rh/Al_2O_3-600 and 1 wt.%Rh/Al_2O_3-900 at 600 °C using He containing a trace amount of O_2 as a carrier gas. The catalysts were pre-reduced with H_2 at 600 °C.

3.3. H_2-TPR and O_2-TPD characterizations

The H_2-TPR and O_2-TPD profiles of the catalysts are shown in Figs. 4 and 5, respectively. The quantified figures of the TPR profiles for the catalysts are shown in Table 3. Each TPR profile shows two reduction peaks at the temperature below 250 °C. These peaks can be attributed to the RhOx species with different extent of interaction with Al_2O_3 [37]. However, the maxima as well as the relative intensity of the two low temperature TPR peaks on the catalysts calcined at 600 and

Table 3
Quantification of the TPR signals for the Rh/Al_2O_3 catalysts

Catalyst	Peak temperature (°C)	Percentage (%)
0.5 wt.%Rh/Al_2O_3-600	117	63.0
	192	28.1
	>600	8.9
0.5 wt.%Rh/Al_2O_3-900	105	3.5
	232	15.5
	>600	81.0
1 wt.%Rh/Al_2O_3-600	112	73.0
	174	12.6
	>600	14.4
1 wt.%Rh/Al_2O_3-900	111	8.8
	210	7.4
	>600	83.8

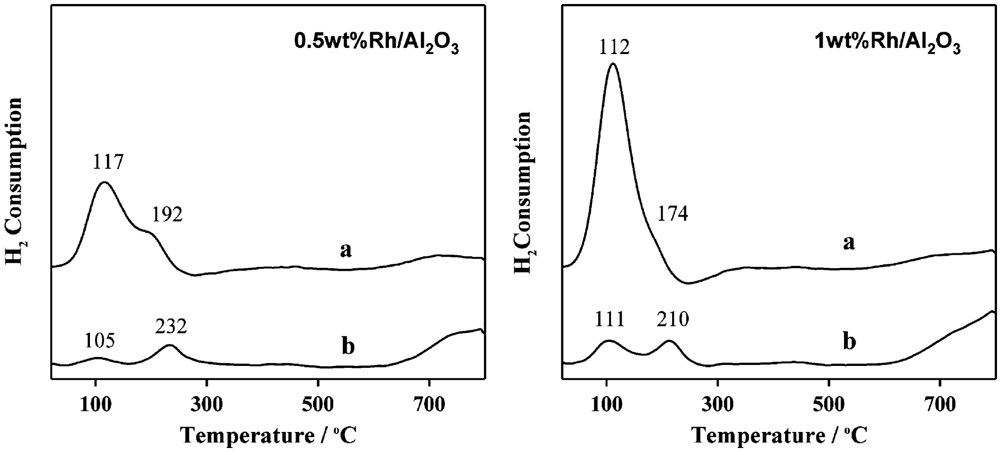

Fig. 4. H_2-TPR profiles of the Rh/Al_2O_3 catalysts calcined at (a) 600 °C and (b) 900 °C. Before experiments, the samples were oxidized with $O_2/He = 1/4$ at 500 °C for 30 min.

900 °C are different, indicating that RhOx species of different nature were formed in the samples calcined at different temperatures. The results of TPR experiment also indicated that, more than 81% of the oxidized rhodium species in Rh/Al_2O_3-900 samples are irreducible by H_2 at temperature below 600 °C. But in the sample calcined at 600 °C, the percentage of the irreducible rhodium species is less than 15%.

The O_2-TPD profile of Rh/Al_2O_3-600 samples shows two desorption peaks with maxima at 880 and 982 °C, respectively (Fig. 5a), while that of Rh/Al_2O_3-900 samples gives only one desorption peak with maximum at 1003 °C (Fig. 5c). The results of O_2-TPD experiment performed over the samples pre-reduced at 600 °C indicate that most of the rhodium species in Rh/Al_2O_3-600 can be reduced by $H_2/Ar = 1/9$ at the temperature below 600 °C (Fig. 5b), while only a small part of the rhodium species in Rh/Al_2O_3-900 is reduced in the same temperature range (Fig. 5d). The temperature maxima of the two O_2 desorption peaks (920, 1036 °C) related to the reducible Rh species on Rh/Al_2O_3-900 (see Fig. 5c and d) are also higher than those on Rh/Al_2O_3-600. The results are in agreement with that of H_2-TPR experiments shown above.

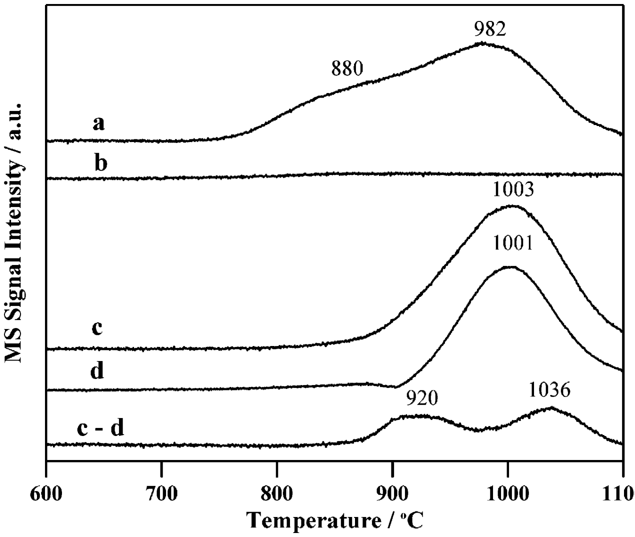

Fig. 5. O_2-TPD profiles of the 0.75wt%Rh/Al_2O_3 catalysts calcined at (a and b) 600 °C and (c and d) 900 °C. Samples were pre-treated with (a and c) $O_2/He = 1/4$ and (b and d) $H_2/Ar = 1/9$ at 600 °C for 30 min.

The results of above H_2-TPR and O_2-TPD characterizations on the Rh/Al_2O_3 catalysts clearly indicate that rhodium species of different nature were formed in Rh/Al_2O_3-600 and Rh/Al_2O_3-900 samples. Compared with the sample calcined at 600 °C, calcination of a Rh/Al_2O_3 sample at 900 °C in the air not only results in the formation of more than 81% of oxidized rhodium species irreducible by H_2 at the temperature below 600 °C, but also modifies reducibility and Rh–O bond strength of the RhOx species that is reducible at lower temperature (<250 °C). These factors would affect the oxygen concentration on the two catalysts under the reaction conditions of POM to synthesis gas and consequently affect the primary products of the reaction.

3.4. High temperature in situ Raman characterization

Although the effects of high temperature (>600 °C) calcination in oxidizing environment on the reducibility of the Rh/Al_2O_3 catalyst has been extensively studied [37–39,41–47], its mechanism is still debated. A number of explanations have been proposed for the nature of high temperature oxidizing interactions including the diffusion of Rh into the bulk of Al_2O_3 [38,41] and the encapsulation of rhodium by alumina [41,44], etc. The formation of a rhodium species strongly interacted with Al_2O_3 and even to the extent of forming a compound with alumina have also been suggested to explain the lose of activity of Rh/Al_2O_3 catalysts after thermal aging or high temperature calcination in an oxidizing environment [37,39,42,43]. However, previous work using extended X-ray absorption fine structure (EXAFS) could not show a rigid local structure around the Rh atom [45,46]. Recently, by using XPS and EXAFS, Dohmae et al. found that Rh was in a highly oxidized state after the oxidation of Rh/Al_2O_3 samples at 1200 °C. The highly oxidized Rh showed a shorter distance between the Rh atom and the next cation than that in Rh_2O_3. The shortened distance agrees with the Rh substitution model

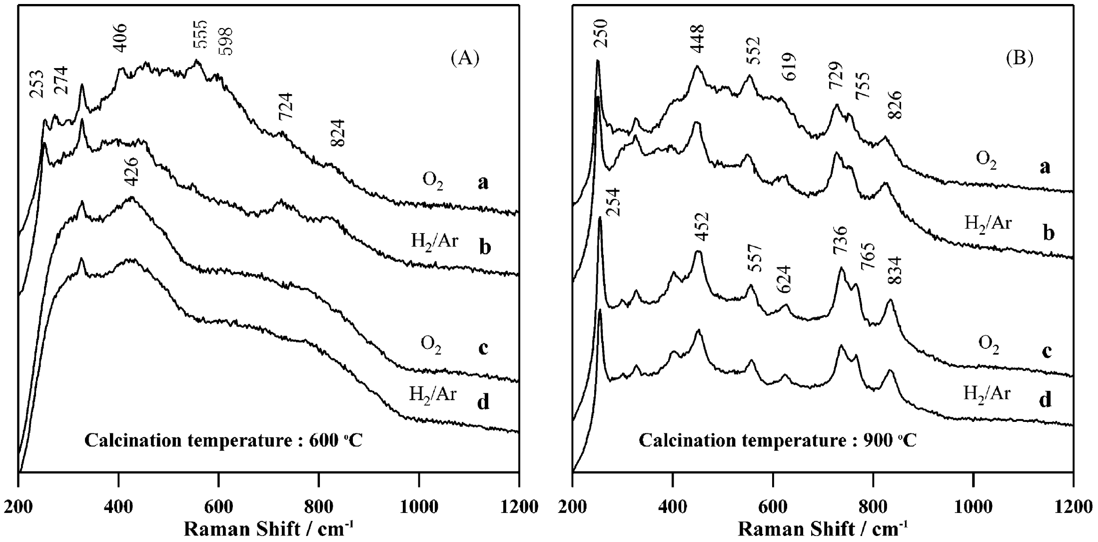

Fig. 6. *In situ* Raman spectra recorded at 600 °C under O_2 and $H_2/Ar = 1/19$ for (a and b) 1.5 wt.%Rh/Al_2O_3 and (c and d) Al_2O_3 calcined at 600 and 900 °C.

[47]. To further elucidate the nature of rhodium species in Rh/Al_2O_3 catalysts calcined at 600 and 900 °C and their chemical state under the reaction conditions of POM to synthesis gas, a comparative study using high temperature *in situ* Raman spectroscopy on Rh/Al_2O_3-600 and Rh/Al_2O_3-900 samples under O_2, H_2/Ar and CH_4/O_2/Ar atmospheres was carried out.

Fig. 6 shows the Raman spectra of Al_2O_3 and Rh/Al_2O_3 catalysts recorded at 600 °C under O_2 and $H_2/Ar = 1/19$ (in the volume ratio) atmospheres. Compared to the Raman spectra of the support calcined at same temperature (Fig. 6A(c and d)), several new bands (253, 274, 406, 555, 598, 724, 824 cm^{-1}) and a broad band between 350 and 700 cm^{-1} were observed in the spectrum of 1.5 wt.% Rh/Al_2O_3-600 recorded under O_2 (Fig. 6A(a)). Among them, the bands at 274, 406, 555 and 598 cm^{-1}, which are not detected in the samples of lower (0.5 and 1 wt.%) Rh loading, are very close to those of the Raman bands of Rh_2O_3 (265, 404, 553, 598 cm^{-1}) prepared by calcination of $RhCl_3{\cdot}nH_2O$ in air at 600 °C, and can therefore be assigned to the supported Rh_2O_3 species. The broad band can be assigned to the RhOx species highly dispersed on the support. The Raman bands of these two species (Rh_2O_3 and RhOx) were readily removed by H_2/Ar mixture at 600 °C (Fig. 6A(b)). Other bands (253, 724, 824 cm^{-1}) in Fig. 6A(a) may have resulted from the oxidized rhodium species strongly interacting with the support. These bands remain unchanged when the sample has been switched to H_2/Ar at 600 °C (Fig. 6A(b)). This observation is in agreement with the results of H_2-TPR experiments shown in Table 3, which indicates that about 15% of the oxidized rhodium species in 1 wt.%Rh/Al_2O_3-600 could not be reduced by H_2 at temperature below 600 °C. The Raman spectra of 1.5 wt.%Rh/Al_2O_3-900 recorded under O_2 and H_2/Ar are shown in Fig. 6B(a and b), respectively. Compared to the spectra of Al_2O_3-900 recorded under the same atmospheres (Fig. 6B(c and d)), the intensity between 350 and 700 cm^{-1} decreased slightly when the oxidized catalyst was switched from O_2 to H_2/Ar. But most of the Raman bands on the sample remain unchanged. The observation is also in agreement with the H_2-TPR results shown in Table 3, which indicates that about 84% of the rhodium in the oxidized form in 1 wt.%Rh/Al_2O_3-900 is irreducible by H_2 at 600 °C. It is interesting to note that the Raman spectrum of 1.5 wt.%Rh/Al_2O_3-900 recorded under H_2/Ar is very similar to the spectra of the Al_2O_3 calcined at 900 °C (Fig. 6B(c and d)), indicating that the surface structure of these samples is very similar. However, compared to the Raman bands of the Al_2O_3 calcined at same temperature, most of the Raman bands on Rh/Al_2O_3-900 shifted to lower frequency by 4–8 cm^{-1}, indicating that local structure of Al_2O_3 slightly changed after the Rh/Al_2O_3 sample being calcined in air at 900 °C. Since the modification of Rh on Al_2O_3 causes only a little shift in the Raman bands of Al_2O_3 and no additional Raman band is detected, it is reasonable to infer that most of the Rh ions on the sample react with (or diffuse into) the support when the Rh/Al_2O_3 sample was calcined in air at 900 °C, leading to the formation of a new rhodium species in which Rh may substitute for the Al site of Al_2O_3. This conclusion is in agreement with the conclusion of Dohmae et al. based on the EXAFS study [47].

Fig. 7 shows the Raman spectra of 1 wt.%Rh/Al_2O_3-600 and 1 wt.%Rh/Al_2O_3-900 catalysts recorded under $CH_4/O_2/Ar = 2/1/45$ when the temperature of samples is raised from 30 to 600 °C. It is found that, as soon as the H_2-reduced Rh/Al_2O_3 catalysts are switched to CH_4/O_2/Ar at the room temperature, a broad band with maximum at 555–560 cm^{-1} is observed (spectra not shown). According to the results of H_2-TPR experiments, this band can be assigned to the RhOx species reducible by H_2 at temperature below 250 °C; this indicates that metallic rhodium species (at least those on the surface) can be oxidized by O_2 in reactant even at room temperature. As the temperature of samples increased, the Raman band of RhOx species on 1 wt.%Rh/Al_2O_3-600 and 1 wt.%Rh/Al_2O_3-900 disappeared at 500 and 550 °C, respectively. The temperatures at which the RhOx species in the catalysts vanishes are in good agreement with the temperatures when the POM reaction over 1 wt.%Rh/Al_2O_3-600 or 1 wt.%Rh/Al_2O_3-900 ignites (see the

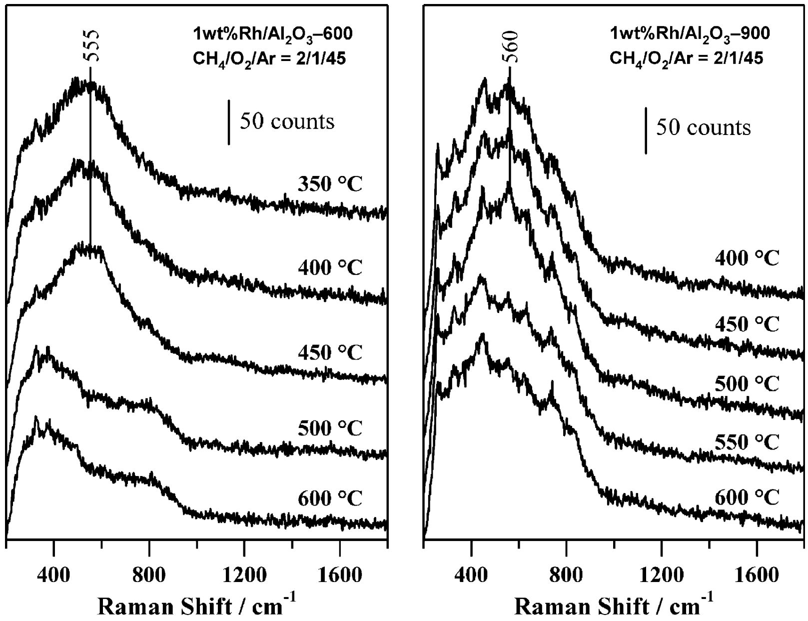

Fig. 7. *In situ* Raman spectra of 1 wt.%Rh/Al_2O_3-600 and 1 wt.%Rh/Al_2O_3-900 catalysts recorded under $CH_4/O_2/Ar = 2/1/45$ atmosphere when the temperature of the pre-reduced samples was raised from 30 to 600 °C.

TPSR profiles shown in Fig. 2). These results indicate that, Rh/Al_2O_3 catalysts in fully oxidized form are mainly responsible for complete oxidation CH_4 to CO_2 and H_2O. The catalysts abruptly changed its oxidation state at the temperature when POM reaction starts. The results of above *in situ* Raman characterization have also provided further experimental evidence that the rhodium species in the Rh/Al_2O_3-900 possesses higher oxygen affinity and are more difficult to reduce than those in Rh/Al_2O_3-600.

4. Conclusions

The significant difference in the catalytic performance of POM to synthesis gas over the Rh/Al_2O_3-600 and Rh/Al_2O_3-900 catalysts can be attributed to the formation of rhodium species of different nature after Rh/Al_2O_3 samples are calcined in the air at 600 and 900 °C. Calcination of Rh/Al_2O_3 in the air at 900 °C causes not only the formation of oxidized rhodium species (irreducible at the temperature below 600 °C) in which Rh may substitute for the Al site of Al_2O_3, but also affect the redox property of the RhOx (reducible at the temperature below 250 °C) in the sample. Compared to the rhodium species in Rh/Al_2O_3-600, the rhodium species in Rh/Al_2O_3-900 possess a stronger Rh–O bond strength and higher oxygen affinity. These factors will affect the concentration of oxygen species on the catalyst surface under the POM reaction conditions and consequently affect the primary products of the reaction on the two catalysts.

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