

Methane adsorption on Rh/Al₂O₃

Dezheng Wang^{b,*}, Oliver Dewaele^{a,1}, Gilbert F. Froment^{a,1}

^a *Laboratorium voor Petrochemische Techniek, Universiteit Gent, Krijgslaan 281, B-9000 Gent, Belgium*

^b *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China*

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Abstract

The rates of CH₄ adsorption on a supported Rh catalyst after different treatments of the surface were measured by means of a temporal-analysis-of-products (TAP) reactor. The catalyst was kept in a well-defined state during adsorption experiments by using a very small pulse size. CH₄ adsorbs on reduced sites. The highest adsorption rate was observed with a catalyst which had undergone an oxygen treatment above 800 K. CH₄ adsorption activity is strongly reduced by the complete removal of oxygen from the catalyst. The results were compared with the adsorption rates of O₂ and H₂O and with the activities for C₂H₆ hydrogenolysis and C₂H₄ hydrogenation. CH₄ adsorption is proposed to be structure sensitive. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane adsorption; Structure-sensitive reaction; Oxygen adsorption; Adsorption rates

1. Introduction

Supported metal catalysts are known to be very active in the conversion of methane via steam reforming or partial oxidation [1,2]. An important metal is Rh because of its high activity in methane partial oxidation and its high selectivity to synthesis gas [2]. The efficient use of a solid catalyst requires a detailed knowledge of the activation of methane. In this report, differences in CH₄ adsorption rates reported in the literature on methane activation over metals are discussed, and a solution is suggested.

The literature data on CH₄ activation on noble metals can be divided into two classes. The first class deals with fundamental studies on single crystal surfaces under high vacuum [3–8]. The second class is concerned with the mechanism and kinetics of reforming and oxidation under industrial conditions [1,2,9–12].

Fundamental studies on the rates of CH₄ adsorption over Rh were described in a series of papers by Stewart and Ehrlich [3] and Brass et al. [13,14]. It is important to note that even in the same laboratory, different rates of CH₄ adsorption were obtained. Brass et al. [13] reported sticking probabilities that were 40 times smaller than those reported by Stewart and Ehrlich [3]. They suggested the difference is due to the form of the Rh catalyst used: a thick Rh film as opposed to a field-emitter tip in the

* Corresponding author. Fax: +86-411-4694447; e-mail: wdz@ms.dicp.ac.cn

¹ Fax: +32-9-264-4999; e-mail: gilbert.froment@rug.ac.be

work of Stewart and Ehrlich. The sticking probability of CH_4 , calculated with an equation from Brass et al. [13], is 2×10^{-5} at 705 K, and is 2×10^{-4} when extrapolated to 1000 K using an activation energy of 11 kcal mole $^{-1}$ as suggested by Brass et al. [14]. The low CH_4 adsorption rate on Rh was confirmed by Yates et al. [15], who found that the CH_4 dissociation rate on Rh is too low to measure.

A high CH_4 adsorption rate is reported in the studies on the oxidation of CH_4 on Rh by Hickman and Schmidt [2,16,17]. Hickman and Schmidt [2] performed a mathematical simulation and reported that experimental data are well fitted using a sticking probability of CH_4 of 0.09. Qualitatively, it can be deduced from their data that the sticking probability of CH_4 above 1000 K is high, and is of the same order of magnitude as the sticking probability of O_2 since the rate of the partial oxidation of CH_4 can be O_2 flux limited. This occurred when the ratio of CH_4 to O_2 exceeded 5 at 1000 K, and when this ratio exceeded 1 at 1500 K. There was a high selectivity to H_2 and CO , which implies a reaction stoichiometry close to 2:1 for $\text{CH}_4:\text{O}_2$. A similar observation was made by Vernon et al. [10] in catalytic oxidation when they reported the effect of the ratio of CH_4 to O_2 used: a threefold overstoichiometry in one reactant effectively induces complete conversion of the other. The sticking probability of O_2 on Rh has been measured as 0.1–0.5 by Yates et al. [18]. A fast adsorption of O_2 on Rh was also confirmed by Padowitz and Sibener [19]. Thus, the sticking probability of CH_4 on Rh in the cases cited in this paragraph must be ca. 0.1 at 1000 K, which is two to three orders of magnitude larger than that measured by Ehrlich et al.

The results from the second class of studies contradict the low sticking probability found in the first class. One possible explanation is that the mechanism of methane activation is different in the two classes of works. This report will argue that the dissociation mechanism is similar in both classes. The difference between the two

classes is proposed to be due to methane dissociation being structure sensitive.

2. Experimental equipment and procedure

The experiments were performed in a temporal-analysis-of-products (TAP) reactor from Autoclave Engineers, USA. This equipment has been described by previous workers [20,21]. Essentially, the apparatus was used as a pulse reactor operated in Knudsen diffusion regime. The pulse sizes were very small relative to the amount of catalyst. In typical experiments, reactant pulse sizes of 3×10^{13} – 1×10^{15} molecules were used over a catalyst bed of 10^{17} – 10^{18} exposed atoms of Rh, that is, the ratio of reactant molecule to exposed atom was 0.05–1%. This minimizes any change to the surface during the experiments. It was verified that the catalyst was not changing with pulses or time by repeating the first train of pulses at the end of each series. Individual pulses were also observed on an oscilloscope with a memory function to make certain there were no systematic variations in the pulse sequence.

The microreactor is a quartz tube 5.6 mm in diameter and 42 mm long. The reactor bed consists of an inert inlet section, a catalyst section and an inert outlet section. It was kept in place by stainless steel wire screens. The inert sections consisted of crushed quartz, while the catalyst section consisted of crushed Rh/ Al_2O_3 catalyst mixed with SiC particles. Particle sizes were 0.25–0.5 mm. The reactor temperature was measured by a chromel–alumel thermocouple housed in an inconel sheath (Thermo Electric, 0.16-mm diameter) positioned in the center of the catalyst bed.

Reactant and product fluxes at the reactor outlet were recorded as a function of time using mass spectrometry (UTI 100C) and a multichannel scaler for signal averaging. The mass spectrometer was tuned to a single mass at a time to avoid dead times resulting from multiplexing.

The Rh/Al₂O₃ catalyst has been described previously [22]. It has a Rh loading of 0.05 wt.% and a BET surface of 153 m² g⁻¹. The H/Rh ratio is about 0.35 as was measured on an Altamira AMI-1 unit by pulse chemisorption at room temperature. The catalyst was oxidized at 873 K for 20 min or 60 min and reduced at 473 K for 20 min before adsorption measurements. These reduction conditions were chosen because EDX analysis showed traces of Ti on the support, and complications could arise due to TiO₂ and the SMSI phenomenon [24]. 473 K is sufficient to reduce Rh [25]. Reduction at higher temperatures and longer times gave reduced hydrogen adsorption capacity. No difference was observed in the hydrogen adsorption capacities nor behavior for CH₄ dissociation between a fresh catalyst sample and a sample of the catalyst that had been used for the partial oxidation of methane up to two weeks in a continuous flow microreactor.

Different pretreatments were applied to the catalyst. The corresponding surfaces will be referred to as Surface 1, Surface 1', Surface 2 and Surface 3. Surface 1' has a different pretreatment from Surface 1 but has a similar activity. Table 1 gives an overview of the different pretreatments. Step 3 in the treatment leading to Surface 3 was applied to remove carbon from the surface. Surface 3 was obtained by pulsing

CH₄ over Surface 2 or Surface 1 until there was minimal adsorption of CH₄. When the CH₄ adsorption rate began to decrease, a slow rate of pulsing, (1 pulse per 10 s) was used to minimize deactivation due to carbon deposition. Adsorbed water on the support can remove deposited carbon if the pulsing rate is slow [22].

The CH₄ and O₂ adsorption rates were measured by means of single pulse experiments over the different surfaces. Methane adsorption is inhibited by adsorbed oxygen at high oxygen coverages [22,23]. At one point in the treatment of the surface, substantial amounts of oxygen are adsorbed on the surface. Some CH₄ pulses were required to remove the adsorbed oxygen before the CH₄ adsorption rate reached its maximum. Then, for small pulses, there was a quasi-steady adsorption activity for many pulses. Only data from this quasi-steady activity region showing the maximum fraction adsorbed were used to derive adsorption rates.

Some experiments were also performed with C₂H₆ hydrogenolysis and C₂H₄ hydrogenation in which C₂H₆ or C₂H₄ was pulsed into a flow of hydrogen at ca. 1 Torr and a flow of 3 × 10⁻⁶ mol min⁻¹. This is similar to a conventional pulse reactor, although at a lower pressure than is usually used. Activity measurements in this mode of operation are reported as conversions based on the appearance of products.

Table 1
Overview of the different pretreatments

Sample	Treatment
Surface 1	1. Fresh catalyst 2. Reduction by H ₂ at 473 K for 20 min 3. Heated to 873 K
Surface 1'	1. Surface 2 2. Heating above 973 K under vacuum
Surface 2	1. Surface 1, Surface 1' or Surface 3 2. Saturation of surface with O ₂ at 873 K or above by pulses or flow of O ₂ 3. CH ₄ pulses until CH ₄ conversion is maximal
Surface 3	1. Surface 2 2. CH ₄ pulses until very low CH ₄ conversion 3. Treatments to remove surface carbon (a) Heated in 1 Torr H ₂ at 473 K for 20 min (b) Heated in 1 Torr 80% H ₂ :20% O ₂ at 473 K for 20–60 min

3. Results

3.1. Adsorption of methane

Rate constants of CH₄ adsorption are reported in Table 2. These were estimated by fitting the reactor model described by previous workers [20,21] to the pulse responses. Surface 2 is about 10 times more active than Surface 1 or 1', but is more than 300 times more active than Surface 3. The catalyst could be cycled between the activities of Surface 1' and Surface 2 by heating in vacuum (or pulsing H₂) above 973 K and pulsing O₂ above 873 K respectively, or cycled between the activities of Surface 2 and Surface 3 by the treatments described in Table 1. The activation energies for CH₄ adsorption are not strongly dependent on pretreatment. The Arrhenius plots for CH₄ adsorption are shown in Fig. 1.

The surface with the highest rate of adsorption was obtained after pulsing oxygen over the

surface at high temperatures, followed by a pulse train of CH₄ (Surface 2). O₂ was pulsed until the O₂ response curves showed little change, which indicates saturated adsorption of O₂. This usually required pulsing three times as much oxygen as there were Rh atoms. When less O₂ was pulsed, the resulting increase in activity was lower. More oxygen, e.g., a flow of oxygen at 1 Torr for up to 5 min, did not give any further change. There was no dependence on the temperature of O₂ adsorption provided the temperature was above 773 K.

3.2. Adsorption of oxygen

The rate of adsorption of oxygen does not depend on the pretreatment or the catalyst temperature. The rate constants of oxygen adsorption are reported in Table 2. These were measured at 300 K in a similar way to those for CH₄ adsorption, but with smaller amounts of catalyst to keep the conversion below 100%.

Table 2
Comparison of the activities of surfaces with different treatments

CH ₄ adsorption ^a	$k_{ad, 723 K} (m^3 kg^{-1} s^{-1})$	Fraction adsorbed at 723 K	Activation energy
Surface 1	0.048	40%	10.8 kcal mol ⁻¹
Surface 2	0.39	90%	10.8 kcal mol ⁻¹
Surface 3	$< 1 \times 10^{-3}$	< 1%	
O ₂ Adsorption ^b	$k_{ad, 300 K} (m^3 kg^{-1} s^{-1})$	Fraction adsorbed at 300 K	
Surface 1	1.53	70%	
Surface 3	1.53	70%	
C ₂ H ₆ Hydrogenolysis ^c		Conversion at 553 K	
Surface 1		0.45%	16.4 kcal mol ⁻¹
Surface 2		11%	19.1 kcal mol ⁻¹
Surface 3		< 0.1% at 673 K	
C ₂ H ₄ Hydrogenation ^b		Conversion at 300 K	
Surface 1		70%	
Surface 2		65%	
Surface 3		40%	

Surface 1 is a reduced as-received catalyst or surface 2 heated at high temperatures. Surface 2 is the catalyst after a high temperature oxygen adsorption after reduction. Surface 3 is the catalyst after complete removal of oxygen.

^aAmount of Rh/Al₂O₃ catalyst used was 0.21 g Rh/Al₂O₃.

^bAmount of Rh/Al₂O₃ catalyst used was 0.024 g Rh/Al₂O₃.

^cAmount of Rh/Al₂O₃ catalyst used was 0.16 g Rh/Al₂O₃.

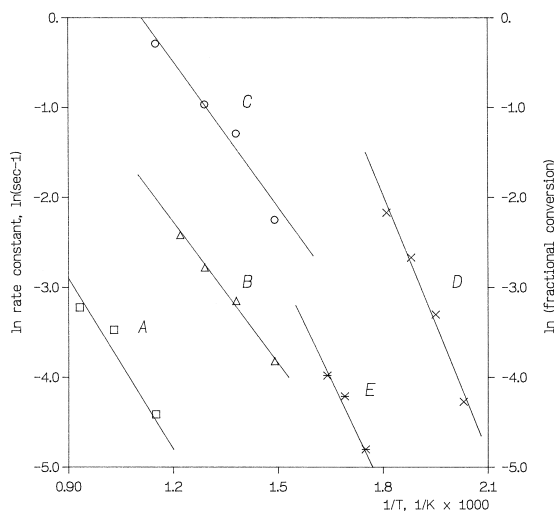


Fig. 1. Arrhenius plots for: (A) a surface that was deactivated by pulsing CH_4 over it (but with the pulsing stopped while the surface still showed some dissociation activity, and which was re-reduced), (B) Surface 1, (C) Surface 2, (D) Surface 2, and (E) Surface 1. Curves A–C are for CH_4 adsorption and use the left y-axis; curves D and E are for C_2H_6 hydrogenolysis and use the right y-axis. Surface 1 is a reduced as-received catalyst or Surface 2 heated at high temperatures. Surface 2 is the catalyst after a high-temperature oxygen adsorption after reduction.

3.3. Dissociation of water

Water strongly interacts with the support. The H_2O pulse responses are too much broadened to be studied. However, H_2 pulses and H_2 responses can be used to study H_2O dissociation because the H_2 response curves may be broadened due to H_2 evolved during the dissociation of H_2O spilled over from the support [22]. The term ‘ H_2O ’ is used as a generic name—the actual adsorbed species are dissociatively adsorbed on the support. A brief description of this process is as follows. Adsorbed H_2O on the support spills over onto the metal and dissociates, producing H_2 and leaving adsorbed oxygen or hydroxyl on the metal. When H_2 is pulsed, a fraction of it adsorbs and reacts with adsorbed oxygen or hydroxyl, thus regenerating surface sites and upon which H_2O spilled over from the support can be dissociated. It is H_2 evolved from this H_2O dissociation that forms the broadening or tail of the H_2 responses.

Thus, the amount of broadening or tail is a qualitative indication of the ability of the surface to dissociate H_2O .

Fig. 2 shows the response curves from H_2 pulses over the three different surfaces when the support was saturated with H_2O . The broadening is most pronounced with Surface 2, and least with Surface 3. This qualitative measure of H_2O dissociation has the same order as CH_4 adsorption, namely, Surface 2 > Surface 1, $1 \gg$ Surface 3.

3.4. Ethene hydrogenation

A minimal amount of catalyst and the lowest possible reactor temperature (300 K) were used to study C_2H_4 hydrogenation by pulsing C_2H_4 in a H_2 flow of $3 \times 10^{-6} \text{ mol s}^{-1}$. Even with this small amount of catalyst, no low C_2H_4 conversions could be achieved, so that only a qualitative interpretation of the results is possible. The latter are also presented in Table 2 and

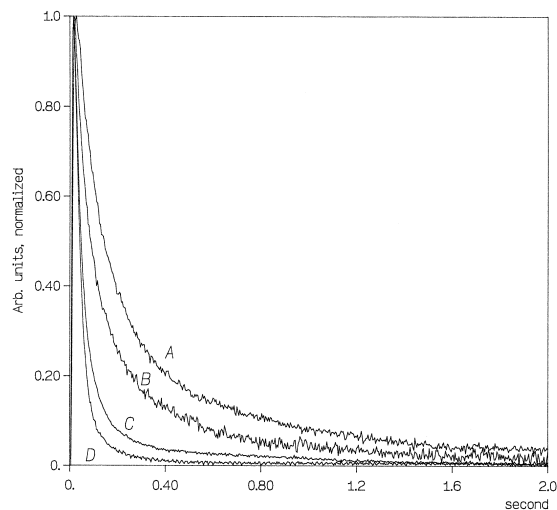


Fig. 2. H_2 response curves from H_2 –He pulses at 473 K over: (A) Surface 2, (B) Surface 1, and (C) Surface 3, and (D) He internal standard. The catalyst had been exposed to a humid atmosphere to saturate the Al_2O_3 support with water, and reduced at 473 K. Surface 1 is a reduced as-received catalyst or Surface 2 heated at high temperatures. Surface 2 is the catalyst after a high-temperature oxygen adsorption after reduction. Surface 3 is the catalyst after complete removal of oxygen.

indicate that the activities are of the same order of magnitude over the three surfaces meaning that the hydrogenation activity does not strongly depend on the pretreatment.

3.5. Ethane hydrogenolysis

Pulsing C_2H_6 over 0.024 g of pretreated catalyst in a H_2 flow of $3 \times 10^{-6} \text{ mol s}^{-1}$ shows a strong dependence of the hydrogenolysis activity with pretreatment. These results are shown in Table 2. Due to the low conversions of C_2H_6 , it can be assumed that the activity is proportional to the conversion [26,27]. The activity of Surface 2 is 20 times higher than that of Surface 1, and estimated to be more than 100 times higher than Surface 3. The activation energies are not strongly dependent on pretreatment. Fig. 1 also shows the Arrhenius plots for C_2H_6 hydrogenolysis.

3.6. Surface 3: carbon deposition and removal

An understanding of the observation that Surface 3 showed very poor activity for CH_4 adsorption is of interest and it is important to check whether this is due to carbon deposits. The following treatments and observations suggest a very low coverage of carbon on Surface 3.

(1) One treatment leading to Surface 3 consisted of H_2 reduction (1 Torr H_2 for 20 min at 473 K). It was observed that subsequent pulses of H_2 from 473 K to 873 K did not produce CH_4 . In separate experiments when carbon was deliberately deposited by C_2H_4 adsorption, subsequent pulsing of H_2 showed CH_4 at and above 473 K. This suggests that the reduction conditions can remove deposited carbon moieties if there were any. (2) Feeding a mixture of 80% H_2 :20% O_2 at about 1 Torr over the catalyst at 473 K resulted in the complete conversion of the O_2 to H_2O . This indicates that the coverage of the surface with carbon is low. (3) The absence of carbon was also verified by the adsorption of C_2H_4 on Surface 3.

The latter was seen to be irreversible and very fast. Its rate was estimated to be of the same order of magnitude as the oxygen adsorption rate. The fractions adsorbed, for both species, were virtually 100% with a fresh catalyst.

4. Discussion

The main observations can be summarized as follows: (1) CH_4 adsorption can be fast and may approach the rate of oxygen adsorption, and (2) there is a dependence on the catalyst pretreatment for CH_4 adsorption, C_2H_6 hydrogenolysis and H_2O dissociation. C_2H_4 hydrogenation and O_2 adsorption do not show a dependence on pretreatment.

One possible explanation for the high rates of CH_4 adsorption that had been considered is that CH_4 dissociation in atmospheric catalytic CH_4 oxidation is due to a gas-phase combustion initiated by surface generated free radicals [28,29].² In this work, CH_4 was adsorbed under vacuum, i.e., in the absence of gas phase oxygen. These conditions were not favorable for chain propagation nor branching and yet a very fast rate of adsorption could be achieved over Surface 2, contradicting gas phase combustion initiated by surface generated free radicals as the mechanism. Other workers in catalytic CH_4 oxidation have accepted that CH_4 dissociation is a surface reaction [2,22,28–30].

The presence of traces of titanium oxide on the support can explain the difference in activity between Surface 1 and Surface 2. Care was taken to avoid hydrogen reduction at high temperatures, which can cause the migration of TiO_x onto the metal. Haller and Resasco [24] had indicated in a review that the presence of hydrogen is necessary for TiO_x migration but their data also indicate that heating under vac-

²The work in Ref. [29] discusses the partial oxidation of ethane, but the comment on surface reaction being dominant should be equally applicable to methane.

uum at 773 K after reduction at low temperatures decreases the ethane hydrogenolysis activity by a factor of two. A loss in activity due to poisoning by TiO_x moieties is possible since the temperature used in the present work is higher. The presence of small amounts of carbon on the active surface can explain the low activity of Surface 3. The treatments which were done to clean the surface of carbon deposits were not entirely satisfactory because the nature of the catalyst and the dependence of the activity on the pretreatment precludes heating under hydrogen or oxygen at high temperatures (> 573 K). If there would be any coverage by TiO_x or carbon, it has to be very low since water formation, C_2H_4 hydrogenation and irreversible C_2H_4 adsorption were fast and the maximum catalyst activity could be rapidly restored by pulsing of oxygen. The results from Stewart and Ehrlich [3], Brass et al. [13] and Yates et al. [15], who found the adsorption of methane over Rh surfaces to be very slow suggest TiO_x or carbon deposition are not the cause of the activity loss. The more likely cause of the large variation in CH_4 dissociation activity are different surface structures depending upon the pretreatments. Then, there is no inconsistency between the differences in observed rates of CH_4 adsorption if the latter is a structure sensitive phenomenon. Furthermore, if small amounts of TiO_x or carbon were present and cause the loss in adsorption activity, this would be additional evidence of the structure sensitivity of methane adsorption.

The increase in methane dissociation activity after an oxygen treatment is another important observation in this work. It was first reported by Lee and Schmidt [31] that an oxygen treatment increases the C_2H_6 hydrogenolysis activity of over four orders of magnitude when oxidation at 873 K was followed by a low temperature reduction at 473 K of Rh/ SiO_2 . Lee and Schmidt suggested that the activity increase was due to the creation of adsorption sites for C_2H_6 by the oxidation–reduction cycle and that both the oxidation and reduction steps were important. The

present work indicates that oxygen adsorption is the important step, in agreement with Buyevskaya et al. [23], who studied the behavior of Rh black in the same reactor type used in the present work and reported that complete reduction results in a catalyst that is inactive for CH_4 adsorption. Buyevskaya et al. proposed that active sites for CH_4 adsorption are special partially oxidized Rh. Central to their argument is that the number of active sites is very low. The data reported in the present work, and in the methane oxidation literature, show that the methane adsorption rate can be almost as high as the oxygen adsorption rate. If the sites for methane adsorption are assumed to be few compared to the sites for oxygen adsorption, one would have the consequence of a methane sticking probability which is much higher than the sticking probability of oxygen. The latter, however, is already close to 1 [18,19]. This leads to the conclusion that the hypothesis of Buyevskaya et al. is not correct.

Two explanations for the increase in CH_4 dissociation activity after the O_2 treatment are possible: the active surface is an oxidized surface or oxygen adsorption changes the surface in a fundamental way. The first explanation was suggested by Garbowski et al. [32] and Buyevskaya et al. [23] and the second by Lee and Schmidt [31] and Burch and Loader [33]. In contradistinction to the first explanation, there is evidence that CH_4 does not easily adsorb on group 8–10 metals in the presence of adsorbed oxygen: negative reaction orders with respect to O_2 , H_2O and CO_2 [1,33,34], direct observations of inhibition by adsorbed oxygen [22,23] and a hysteresis due to low rates over an oxidized catalyst [35]. Accordingly, some authors accept that the active site for CH_4 adsorption is a reduced metal surface [22,23,28]. It was shown by Wang et al. [22] that the CH_4 adsorption rate can be high on a surface that has a very low O coverage. Their data indicate that CH_4 can be rapidly dissociated on a surface containing very little surface oxygen, and that the rate of CH_4 adsorption is independent of oxygen coverage if

this is lower than the coverage where oxygen inhibits CH_4 adsorption. Also, the results in the present work on C_2H_6 hydrogenolysis, evidently carried out in a H_2 atmosphere, also indicate that the active surface is a reduced surface since there is a correlation between the C_2H_6 hydrogenolysis activity and the CH_4 adsorption rate.

Both observations—that CH_4 adsorbs on a reduced surface and that a high temperature O_2 treatment increases the rate of CH_4 adsorption—indicate that the surface morphology determines the rate of adsorption. The low loading of the catalyst used here did not permit any physical characterization of the surface, but C_2H_6 hydrogenolysis and H_2O dissociation are useful as chemical characterizations of the surface structure. It is accepted that C_2H_6 hydrogenolysis is structure sensitive [36,24] and there is strong evidence that H_2O dissociation [37] is structure sensitive over Rh. It is quite likely that a surface roughening accounts for the accelerated CH_4 adsorption. Although no mechanism for how the roughening occurred can be ascertained yet, a useful observation here is that oxygen adsorption at a high temperature is a treatment that gives accelerated CH_4 adsorption. Lee and Schmidt [31] suggest that roughening occurs when large crystallites are broken up into small ones during reduction. Burch and Loader [33] suggest a reconstruction that gives more steps and kinks.

5. Conclusions

CH_4 adsorption on a Rh catalyst is structure sensitive: the rates of dissociative CH_4 adsorption cover quite a range. CH_4 adsorption is accelerated by oxygen adsorption above 800 K. The highest adsorption rate occurs on a reduced surface, although some oxygen has to be present. Oxygen adsorbed at high temperatures changes the surface morphology. CH_4 adsorption is significantly decreased by the complete removal of oxygen from the catalyst.

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