

Electronic structure and adsorption properties of precious metals and their oxides: Density functional calculations

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Abstract

The electronic structure of bare MeO and Me₂ dimers (with Me = Rh or Pd) has been calculated together with their interaction with a methane molecule for various adsorption geometries by means of quantum chemical density functional methodology. It has been found that the strongest non-dissociative adsorption of methane occurs in a bridging position on a palladium dimer accompanied by very strong activation of a C–H bond and a negligible energy barrier for the bond scission. Any adsorption on other systems was weaker and the barrier higher. This could be ascribed to the absence of repulsive 5s electrons in the case of palladium dimer. The strongest stabilization of the dissociated hydrogen was found, however, to occur on PdO. These results may be useful in explaining experimental findings which indicated that a supported palladium catalyst, showing subsequently metallic and oxidized phases is a very efficient medium for methane combustion.

Keywords: Electronic structures; Rhodium oxide; Palladium oxide; Adsorption; Methane

1. Introduction

Methane activation on adsorption on supported noble metals and metal oxides has long been an intriguing subject for both experiment and theory [1]. One of important areas where this process should be of great importance is efficient catalytic combustion of hydrocarbons in clean flame burners with lowered reaction temperature for environmental protection [2]. Among proposed catalytic systems the superiority of palladium as a catalyst for complete oxidation of methane to carbon dioxide and water

has been well known for years, the nature of the active sites, however, has still been the subject of debates and numerous studies [3,4]. Experimental research revealed that catalytic combustion is a structure sensitive reaction, one of the assumptions is that high efficiency of palladium may be related to its ability to dissociate oxygen molecules by forming a surface oxide. The existence of bulk PdO, however, is not a prerequisite for obtaining an active catalyst [3], it is even considered as a poorly active phase while PdO deposited on metallic palladium constitutes a very active phase in supported oxidized palladium catalysts [4]. It has been shown that periodic decomposition of palladium oxide to metallic Pd and re-oxidation occurred during the

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catalytic methane combustion over Pd catalysts in temperature exceeding 800°C in accord with observed hysteresis in the reduction–reoxidation process [3] while negligible activity of metallic palladium towards methane combustion has also been reported [5].

The ability to activate the C–H bond in a hydrocarbon should certainly be a crucial step in such a process as has already been shown in the case of catalytic reduction of nitrogen oxides by methane [6]. This activation is very efficient on metallic palladium where such processes as the dissociation of molecular hydrogen or C–H bonds in hydrocarbons may easily occur [1]. The metallic palladium itself, however, does not exhibit high activity in the methane combustion. Thus dissociation and reactivity of oxygen must obviously be another factor providing high efficiency of the process. In our previous work we have studied theoretically simple palladium — oxygen systems which could be regarded as crude functional models of metallic and oxidized palladium centers in the process of methane activation. In particular adsorption, activation and scission of the C–H bond on palladium dimer, palladium oxide diatomic and Pd₂O clusters were investigated by means of quantum chemical DFT methodology [7,8].

Much less is known about rhodium based supported species although rhodium is an element which is used as a component of many catalysts. In heterogeneous catalysis rhodium is the metal normally used to enhance nitrogen oxides reduction in palladium based three-way catalysts. This is related to the fact that rhodium readily dissociates nitric oxide to nitrogen and oxygen, and nitrogen is not converted to undesired ammonia [9]. Partial oxidation of methane to carbon monoxide and hydrogen was also reported to occur at 700°C on rhodium supported on vanadia [10]. Rh/Al₂O₃ catalysts were also studied in the reduction of NO by CO in which a strong accelerating effect of the presence of hydrogen was observed, and in decomposition of N₂O, in which it was found to

be very active [11]. At low temperatures oxygen is adsorbed on noble metals surfaces with a very high sticking coefficient in molecular form, oxygen molecules lying parallel to the surface. Studies of the interaction of oxygen with Rh(100) and polycrystalline Rh at 400–600°C showed that at a pressure higher than 10⁻¹ Pa, a Rh₂O₃ layer was formed independently of the surface structure [12]. An interesting behavior of rhodium was recently reported [13]. When alkyl radicals, formed in situ by decomposition of alkyl iodides, were introduced on the oxygen-covered Rh(111) surface, they reacted along two parallel reaction pathways: either the surface oxygen atoms abstracted hydrogen from the alkyl radicals, or they bound these radicals forming transient alkoxides, which subsequently underwent dehydrogenation to form aldehydes or ketones. On clean Rh(111) surface the alkyl radicals adsorbed and decomposed with the formation of carbon deposit.

It seemed thus worthy to perform quantum chemical calculations on small rhodium based clusters in order to compare their properties with those of palladium systems in hope to reveal some aspects of the mechanism of hydrocarbons activation on varying media and select properties responsible for high activity of precious metals in catalytic oxidation. In the present paper we report DFT calculations on the electronic properties of rhodium oxide, rhodium dimer and the methane adsorption. These results might be then compared to analogous palladium systems. We hope that even if such simple model calculations cannot be claimed to mimic actual catalytic sites, they might reveal important information about some features making the catalytic system efficient.

2. Computational details

2.1. Calculation conditions

All DF calculations presented in this paper were carried out using the Kohn–Sham method-

ology as implemented in the DMol program package [14] of BIOSYM Technol. The calculations were performed at two levels of the approximations for the exchange-correlation potential. For the single SCF energy calculations and geometry optimizations we used local density approximation with Janak–Moruzzi–Williams (JMW) functional [15]. To calculate more accurate energy values we employed the Becke–Lee–Yang–Parr (BLYP) nonlocal functional [16] for the optimized geometry obtained from local level calculations. As the basis set, we chose double numerical basis functions together with polarization functions (DNP) for all the calculations which is of Gaussian 6-31G** quality, standard basis set in quantum chemistry and has been already found sufficient to describe adsorption and methane activation on the Ga site in zeolites [10].

Potential energy curves for diatomic clusters were generated in both approximations for each electronic state from point-wise calculations for a grid of 8–10 points around the equilibrium geometry. Optimum bond distances, dissociation energies and other spectroscopic constants have been obtained from the potential fitting procedure by the appropriate software [17] at each level of the approximation. Present results have confirmed our previous findings that the geometry is better reproducible at the local level while energetical parameters require nonlocal corrections. Thus geometry optimizations for methane adsorbed on model clusters were performed only within local approximation with the aid of analytical gradients using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm implemented in the software. We recognized the optimized geometries when the norm of the gradient vector was smaller than 0.001 a.u.

2.2. Models for DF calculations

The simplest system where the interaction of a hydrocarbon molecule with a metal oxide can be investigated is the metal oxide MeO diatomic

molecule. Although it can be hardly taken as a realistic model of a bulk oxide or oxidized metal catalyst, it offers wide possibility of deep studies on the electronic structure of the system composed of a cluster and a hydrocarbon molecule and its evolution along the adsorption and prospective dissociation processes, within high-level quantum chemical methodology. Our previous studies on the electronic structure of palladium systems and the methane activation [7,8] have clearly indicated that only detailed knowledge of the electronic state of the system, be it a simple diatomic cluster, may bring some insight into the intricate mechanism of a hydrocarbon adsorption and the activation of a carbon–hydrogen bond. On this basis we have successfully drawn qualitative conclusions regarding some factors governing catalytic combustion of methane on an active site in a supported metal catalyst. In the same way the differences in behavior of oxidized and metallic phases may be studied on the basis of the interaction of methane with a metallic dimer [8]. Such an approach might be further justified since the structure of the surface in a Me/Al₂O₃ catalysts (where Me = Pd, Rh, Pt, etc.), which are often used for catalytic combustion of hydrocarbons, is still not well known and direct modelling seems not to be possible.

Thus in this work the interaction of a methane with diatomic clusters: PdO, Pd₂, RhO and Rh₂ will be assumed as a crude model interaction of a hydrocarbon with metallic and oxidized sites in supported metal catalysts. First, the detailed structure of diatomic clusters will be discussed on the basis of the fitted potential energy curves. Next the adsorption of methane over the clusters will be discussed. Here, the approximate potential energy curves with respect to a distance carbon–metal atom or a carbon–midpoint in a cluster bond have been generated with fixed geometry of the reactants. Starting from the approximate energy minima, the geometry of the system has been then fully optimized. Potential energy surfaces close to minima have been scanned for various electronic states as it was

already shown in the study on palladium systems that the basins for substrates, products and the transition state might belong to different surfaces and the surface crossing might be an important factor in determining energetical properties of the process.

3. Results of calculations

3.1. Electronic states of diatomic clusters

Details of the electronic structure of PdO and Pd₂ have been already given elsewhere [7,8] and we will only briefly recall our results here. Electronic structure of the rhodium oxide and rhodium dimer has not been studied previously to large extent and we will report our results here in more detail. Entire potential energy curves for diatomic species have been subjected to both local and nonlocal DFT calculations. Such approach was a routine in our previous studies [7,8] since it was advisable to fully include nonlocal corrections in one-dimensional cases. Table 1 presents the results of our calculations for the quartet ground state, and selected doublet states of the RhO molecule. In the table the equilibrium bond distance R_e (Å), the dissociation energy D_e (eV), the vibrational energy between the two lowest vibrational levels ω_e (cm⁻¹), the rotational constant B_e (cm⁻¹), and

the excitation energy from the ground state (cm⁻¹) are listed. The dissociation energy has been calculated with respect to the triplet oxygen and the ⁴F atomic state of rhodium. We can see from the table that the ground state is the $\pi^2\sigma^1^4\Sigma^-$ open shell quartet, in agreement with the previous calculations of Siegbahn [18]. It is also clear that our DF calculations within nonlocal approximation give much better dissociation energy than correlated traditional ab initio calculations. This is not the case with respect to bond distances where nonlocal potentials overestimate bond lengths compared to as well experimental as other ab initio values [19]. The same was found true in the case of other transition metal oxides and homonuclear dimers [7,8,19] thus we feel authorized to strongly advertise DFT methodology as a reliable tool for calculation of energetical effects. However, mixed calculational procedure seems to be justified for larger systems. Geometrical parameters are expected to be of acceptable accuracy already at the local level whereas including nonlocal corrections leads to worsening of their values. Therefore geometry optimizations for composed systems would be conducted with the local potential. Table 1 already indicates that the sequence of electronic states as well as state separations are independent of the assumed approximation which again might serve for justifying validity of local results in qualitative comparisons for larger systems. Among states originating from doublet-coupled $\pi^2\sigma^1$ configuration only the ²Δ state can be expressed as a single determinant and thus may be the subject of rigorous DF calculations. It is located about 9400 cm⁻¹ above the ground state and displays very similar spectroscopic properties. Other two $\pi^2\sigma^1$ states, ²Σ⁺ and ²Σ⁻, may be expressed only by a combination of determinants. Our estimation from the sum rules places these states about 5900 cm⁻¹ and 9700 cm⁻¹ above the ground state, respectively, with the bond distance by 0.01 Å shorter. The last low-lying doublet is the ²Π state coming from π^3 configuration. It is located only 5800 cm⁻¹ above the

Table 1
Properties of electronic states of RhO: optimum bond distance, dissociation energy, vibrational frequency, rotational constant and excitation energy (L-with local potential, NL-with nonlocal corrections)

		R_e (Å)	D_e (eV)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	Δ (cm ⁻¹)
⁴ Σ ⁻	L	1.75	5.58	805	0.397	
	NL	1.80	4.54	727	0.375	
	Ref. [17] exp	1.74	3.32	4.2		
² Π	L	1.75	4.86	831	0.397	5807
	NL	1.80	3.81	743	0.376	5807
² Δ	L	1.75	4.41	818	0.400	9436
	NL	1.80	3.38	740	0.378	9275

ground state, has the same equilibrium bond distance and similar vibrational frequency. We will see in forthcoming paragraphs that the properties of the ground state and the first excited doublet have substantial influence on the adsorption and dissociation of a methane molecule.

In the case of the PdO the ground state was found to be the triplet $^3\Pi$ coming from $\pi^3\sigma^1$ configuration. It has been shown that the properties of singly occupied SOMO composed mainly of $s-d_0$ hybrid on palladium was responsible for relatively strong collinear adsorption of a methane molecule. The other SOMO was of π character, composed of the antibonding combination of metal d_π and oxygen p_π orbitals. This seemed to support bridging adsorption of a methane on PdO molecule. The same features have been found here for RhO oxide thus we can expect similar geometries of adsorption modes with comparable strengths, namely the strongest collinear adsorption and a weakly bonded bridging mode.

Rhodium dimer might be described as a relatively strongly bonded molecule compared to the $^1\Sigma_g$ palladium dimer found by us the most stable. The assignment of highly open-shell electronic states is even more difficult for Rh_2 than for Pd_2 [20,21]. We have established its lowest electronic state as the quintet $^5\Delta$ coming from $\delta_d^* \pi_d^* \pi_d^* \sigma_s^1$ open-shell electronic structure. The equilibrium bond distance of 2.30 Å and the dissociation energy of 2.53 eV may be compared with the values of $R_e = 2.70$ Å and $D_e = 0.82$ eV for Pd_2 dimer. In the closed-shell palladium dimer bonding and antibonding interactions merely cancel whereas in the rhodium dimer antibonding counterparts to π_d orbitals are only partially occupied. Moreover, $4d \rightarrow 5s$

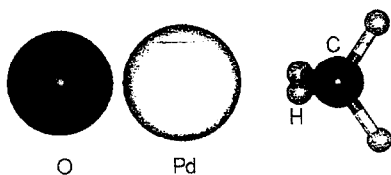


Fig. 1. The model for collinear adsorption of methane on PdO.

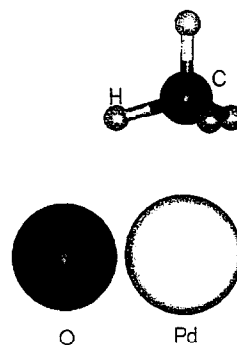


Fig. 2. The model for metal on-top adsorption of methane on PdO.

electron promotion has been calculated as ca. 0.1 electron in the former molecule while it is increased to one electron in the latter. Thus repulsive interaction with 5s electrons should make the adsorption of methane weaker in the case of Rh_2 .

3.2. Methane adsorption

According to the procedure described in computational details various adsorption modes defined by the choice of the reaction coordinate have been investigated in the present work. All geometry optimizations were done here within the local approximation. The investigated modes were the following: (i) collinear adsorption (C–Me distance selected as a working coordinate, collinear approach, see Fig. 1), (ii) metal on-top (C–Me distance defining the reaction coordinate, perpendicular approach, see Fig. 2), (iii) bridging adsorption (the distance between carbon atom and the center of dimer bond selected, see Fig. 3) and finally the dissociated mode (iv),

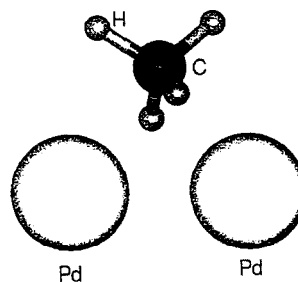


Fig. 3. The model for bridging adsorption of methane on Pd_2 .

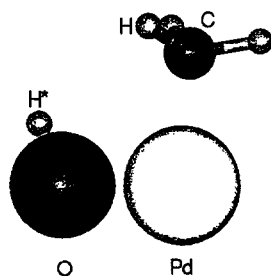


Fig. 4. Optimum geometry of the dissociative adsorption of methane on PdO.

with a methyl bonded to a metal atom and a hydrogen bonded to an oxygen in the case of the oxide (Fig. 4) or moving around the metal dimer after the scission of the C–H bond (Fig. 5). In addition to these systems we attempted to search for the transition states in the process of the C–H bond scission found strongly exothermic in the case of oxides and slightly exothermic in the case of metal dimers. The procedure consisted in step-wise increasing the C–H bond length and optimizing other geometrical parameters (an analogue of minimum energy path). The starting point was the bridging adsorption found previously the most promising for the activation of a carbon–hydrogen bond. For all systems stable preadsorbed states have been spotted, as well for collinear as for bridging geometries. Introducing nonlocal corrections lowered the stability, the systems, however, remained bound. Nevertheless, the adsorption should be viewed as weak with no strong bonds formed. The spin state for all preadsorbed species was found to be the same as the one for substrates. Low spin adsorption complexes were

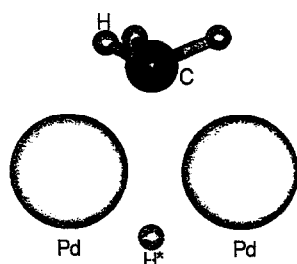


Fig. 5. Optimum geometry of a methyl and a hydrogen species on Pd₂.

placed at much higher energy for PdO, RhO and Rh₂ while on palladium dimer the singlet was even more stabilized than for a separate dimer. In the case of oxides and rhodium dimer increasing the C–H bond towards the transition state brought the two spin surfaces closer to each other. Finally, their crossing must have been expected in the vicinity of TS as all dissociated products were placed on low spin surfaces. Thus direct rigorous calculation of the transition state as the maximum along the ‘softest’ reaction coordinate would be virtually impossible. We are not claiming our result to be the true transition state, its approximate structure indicates that efficient attractive interaction should be switched on between the dissociative hydrogen and the oxygen at the distance of about 1.5 Å and the metal at ca. 1.7 Å, with the C–H bond stretched to 1.4–1.5 Å. The hydrogen remains slightly positive on oxides and bears small negative charge on metal dimers.

The results of the calculations are shown in Table 2. The table lists the relative energies (in kcal/mol) of various adsorption modes of a methane on MeO and Me₂ (where Me = Pd or Rh). All listed energies were obtained within the local DFT approximation as they are intended only for comparative analyses. The energies were calculated with respect to the separate methane molecule and the ground state dimer. Appropriate energies for bare metal atoms taken from Ref. [22] are also included in the table for comparison. The selected row in Table 2 may

Table 2

Relative energies (in kcal/mol) of various adsorption states of methane on Pd and Rh systems (with respect to separate methane and the appropriate dimer: all results in local exchange-correlation approximation)

	Co-linear	On-top	Bridge	TS	Dis
PdO	–20	–9	–6	+5	–53
Pd ₂	–17	–24	–26	–23	–37
RhO	–19	–6	–4	+10	–33
Rh ₂	–11	–7	–6		–25
Pd		–4		+16	+9
Rh		+6		+14	–5

be regarded as mapping energetical evolution of the system along the assumed reaction coordinate which describes the approach of a methane towards the selected system, its adsorption and dissociation. After inspecting the table the following features of the adsorption process may be inferred:

(i) In the case of palladium oxide, strong adsorption occurs in the collinear position. There is also a shallower energy minimum for the bridging position but it requires activation with respect to the most stable one. Both adsorption modes are bound relatively weakly, the spin coupling is the same as in an isolated PdO dimer, that is the triplet. Further activation of the system is, however, very cheap, small change in geometry leads to the change of the spin state to singlet and costs only a few kcal/mol. This singlet state is located already on the dissociative potential energy surface and thus C–H bond scission occurs spontaneously and the stable final product is obtained.

(ii) Rhodium oxide behaves in a very similar way, shows comparable preliminary collinear adsorption and activation towards bridging adsorption and transition state. The difference, however, arises in the vicinity of the transition state. Here the spin transition cost mounts to extra circa 10 kcal/mol which would rise the barrier and indicate lower stability of the final product.

(iii) In the case of palladium dimer the best adsorption geometry is apparently the bridging

one, this is the strongest non-dissociative adsorption among the studied systems. Here, very strong activation of the C–H bond is already observed (see Table 3) and the scission of the bond costs only 3 kcal/mol. The final product, however, is only 11 kcal/mol more stable than the adsorption complex while this difference amounts to 33 kcal/mol for the oxide.

(iv) Rhodium dimer has been included in the table although the calculations of the transition state have not yet been fully completed. It does not exhibit any position for strong adsorption of a methane, in accord with the predictions coming from its electronic structure. A methane molecule binds weakly in collinear position, other positions are higher in energy, in addition no significant activation of the C–H bond may be noticed (see Table 3). Also the dissociated complex has the lowest stability among studied dimers.

(v) Bare metal atoms show similar important features towards adsorption of a methane and formation of the insertion products into the C–H bond. The discussion of these properties in metal atoms and dimers bears similar qualitative features regarding the interdependence between the electronic state and reactivity. In the case of palladium atom with closed-shell d^{10} electronic structure no repulsive 5s electrons are present thus the adsorption complex is relatively stable but the insertion product is not. Rhodium atom has the open-shell electronic d^8s^1 configuration and due to repulsion with 5s electrons the ad-

Table 3

Selected bond distances and the charge on active hydrogen for preadsorption or dissociative adsorption of methane on studied systems and the effective cluster \rightarrow methane charge transfer during dissociation

	Pd ₂		PdO		RhO		Rh ₂	
	ads	dis	ads	dis	ads	dis	ads	dis
R_{Me-C} (Å)	2.20	2.14	2.36	1.99	2.43	1.99	2.44	1.99
R_{C-H} (Å)	1.23	–	1.13	–	1.13	–	1.13	–
R_{Me-H} (Å)	1.80	1.60	2.02	–	2.06	–	2.02	1.55
R_{O-H} (Å)	–	–	–	0.99	–	0.99	–	–
Q_H (e)	–0.06	–0.15	+0.02	+0.11	+0.04	+0.13	+0.03	–0.06
CT (e) (ads-dis)	+0.23	–	–0.07	–	–0.07	–	+0.15	–

sorption complex is unstable but the insertion product has substantial stability.

In the case of dimers, only Pd₂ has no 5s electrons in the ground state and all reaction intermediates lie on the same spin-surface thus both the adsorption complex and the dissociation product are stable. For rhodium dimer in its high-spin ground state the adsorption complex is less stable due to repulsive interaction with Rh 5s electrons while the dissociation complex lies on a low-spin surface and may be reached only via prerequisite spin transition. There exist no quantitative experimental data regarding the adsorption of methane on precious metals. High stability of the bridging adsorption mode on Pd₂ has, however, been predicted theoretically for CO adsorbed on a Pd₄ cluster [21]. Also IR and TDP experiments were reported to indicate that CO adsorbs on palladium at 3-fold and bridging sites at intermediate coverages. The top site is only populated at high coverage on palladium while it is first occupied on Rh(111) surface [21]. These findings might be taken as some indication that our results on adsorption of methane on palladium and rhodium systems should also be reasonable.

4. Discussion and conclusions

Table 3 lists selected properties of the studied systems for the dissociation product (DIS) and the most stable preadsorption (ADS) which is in the collinear position on a metal atom in all cases apart from Pd₂ where it is the bridging position. The dimers are arranged in the order of increasing stability of the preadsorbed complex. The distances between the metal and the carbon atoms or between the active hydrogen and the carbon, metal or oxygen atoms are displayed. In addition the charge on active hydrogen and the value of the charge transferred from the cluster to the adsorbed species during the dissociation process (positive sign indicates the charge transfer from the cluster) are also given in the table. The charges have been calcu-

lated according to Hirschfeld definition [23]. Chemisorptive bonding of a methane molecule with a metal atom is generally mediated by hydrogens with the most pronouncing effect and the shortest metal–hydrogen bond displayed for palladium. The strongest methane adsorption and activation of hydrogen on palladium dimer may be fully confirmed here in accord with high affinity of palladium towards hydrogen. Rhodium dimer occupies the position of the least active agent. The difference between palladium and rhodium with respect to their affinity towards hydrogen might be also related to their metallic properties. Since bonding and antibonding interactions within the palladium dimer are weak thus the splitting of the fully occupied d ‘band’ is small (ca. 2 eV) with the empty s ‘band’ lying 0.8 eV higher. In the case of rhodium dimer partially occupied d and s ‘bands’ overlap and span over energy range wider than 4 eV. Thus we can expect easier bond formation and localization of electrons in the former case. The hydrogen dissociated on a metal bears negative charge and the overall electron transfer occurs from the metal dimer, however, in the case of rhodium the effect is small. The effect is almost negligible on oxides where slightly positive hydrogen is finally strongly covalently bonded within the OH group.

According to our previous findings [7,8] and other authors [22] two main factors influence the height of the activation barrier and the reaction energetical effect: moderate adsorption strength in the entrance channel and strong bonds formation in the reaction channel. This implies that in the case of oxides we should expect moderate barriers and high exothermicity. Indeed, in the case of oxides the product is very stable and the adsorption is only moderately strong which manifests itself by the change of spin state in the transition complex, from the quartet (RhO) or triplet (PdO) to doublet or singlet, respectively. The same was found true by Siegbahn et al. [22] in the case of bare rhodium atom. It imposes substantial height of the barrier increased by prerequisite spin transi-

tion from the high spin state to the low spin state of the system. Palladium atom is an exception among late second row transition metals and does not show such spin transition.

For metal dimers the dissociated methyl and hydrogen do not form strong bonds and the reaction exothermicity is smaller than for appropriate oxides. In the case of the palladium dimer it manifests itself also in disappearance of the spin transition and all adsorption modes lie on the same spin surface. As the adsorption of methane is also moderate, the dissociation barrier is rather low (a few kcal/mol) but the bonds in dissociated complex are weak, thus the reverse recombination reaction seems to be of comparable probability. For rhodium dimer the adsorption complex and the product lie on different spin surfaces thus although due to repulsive 5s electrons adsorption is weak, required spin-flip would raise the dissociation energy barrier.

The most promising situation would be invoked when both phases, metallic and oxidized one, were present on the catalyst surface, which is realized in supported oxidized palladium catalyst. We have supported this hypothesis in our previous work concerning the activation of methane on PdO, Pd₂ and mixed Pd₂O clusters [8]. Here from the comparison of the properties of rhodium and palladium small systems we can infer more information on the properties of the catalyst components prerequisite to assure its high activity. From data listed in Table 2 we can compare the overall probabilities of the processes occurring on mixed centers. In the case of palladium systems the most favorable predissociative adsorption mode is the bridging adsorption on palladium dimer. In this position a methane molecule becomes strongly activated and the scission of the C–H bond occurs with almost no barrier. After dissociation it is the complex of PdO with methyl and hydrogen fragments which is the most stable state of the system. Thus in the presence of oxygen the process in question should have low activation barrier and high efficiency of methane degrada-

tion. In the case of rhodium system the preferred adsorption is the collinear mode on RhO while the one on rhodium dimer cannot concur as it is fairly weak and brings not so distinct methane activation. Thus we may expect higher activation barrier in this case and lower efficiency of the methane combustion on rhodium catalysts.

References

- [1] J.A. Davies, P.L. Watson, J.F. Liebman and A. Georg (Eds.), *Selective Hydrocarbon Activation* (VCH Publishers, New York, 1990); A. Fontijn (Ed.), *Gas Phase Metal Reactions* (Elsevier, Amsterdam, 1992).
- [2] H. Arai and M. Machida, *Catal. Today* 10 (1991) 81.
- [3] Y. Li and J.N. Armor, *Appl. Catal. B* 3 (1994) 275; R.J. Ferrauto, M.C. Hobson, T. Kennelly and E.M. Waterman, *Appl. Catal. A* 81 (1992) 227.
- [4] E. Garbowski, C. Feumi-Jantou, N. Mouaddib and M. Primet, *Appl. Catal. A* 109 (1994) 277; N. Mouaddib, C. Feumi Jantou, E. Garbowski and M. Primet, *Appl. Catal. A* 87 (1992) 129; P. Briot and M. Primet, *Appl. Catal.* 68 (1991) 301.
- [5] R. Burch and F.J. Urbano, *Appl. Catal. A* 124 (1995) 121.
- [6] R. Vetrivel, M. Kubo, H. Himei, E. Maruya, M. Katagiri, E. Broclawik and A. Miyamoto, in: Y. Izumi, H. Arai and M. Iwamoto (Eds.), *Science and Technology in Catalysis 1994, Studies in Surface Science and Catalysis, Vol. 92* (Kodensha, Tokyo, 1995); E. Broclawik, H. Himei, M. Yamadaya, M. Kubo, R. Vetrivel and A. Miyamoto, *J. Chem. Phys.* 103 (1995) 2120; H. Himei, M. Yamadaya, M. Kubo, R. Vetrivel, E. Broclawik and A. Miyamoto, *J. Phys. Chem.* 99 (1995) 12461.
- [7] E. Broclawik, R. Yamauchi, A. Endou, M. Kubo and A. Miyamoto, *J. Chem. Phys.* 104 (1996) 4048.
- [8] E. Broclawik, R. Yamauchi, A. Endou, M. Kubo and A. Miyamoto, *Int. J. Quantum Chem.*, in print.
- [9] A. Sandell, A. Nilsson and N. Martensson, *Surf Sci.* 241 (1991) L1.
- [10] K. Kunimori, S. Umeda, J. Nakamura and T. Uchiyama, *Bull. Chem. Soc. Jpn.* 65 (1992) 2562.
- [11] K. Dumpelmann, N.W. Cant and D.L. Trimm, *Catal. Lett.* 32 (1995) 357; J. Oi, A. Obuchi, A. Ogata, H. Yagita, G.R. Bamwenda and K. Mizuno, *Chem. Lett. Jpn.* (1995) 453.
- [12] A.N. Salanov and V.I. Savchenko, *Kinet. Katal.* 35 (1994) 780.
- [13] C.W.J. Bol and C.M. Friend, *J. Phys. Chem.* 99 (1995) 11930.
- [14] DMol version 2.3.5 San Diego: Biosym Technologies (1993).
- [15] V.L. Moruzzi, J.F. Janak and A.R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
- [16] A. Becke, *J. Chem. Phys.* 88 (1988) 2547; C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B* 37 (1988) 786.
- [17] R.J. Leroy, Program Manual for LEVEL. Univ. of Waterloo, Chem. Phys. Res. Report CP-330 (1992).

- [18] P.E.M. Siegbahn, *Chem. Phys. Lett.* 201 (1993) 15.
- [19] E. Broclawik, in: J.M. Seminario and P. Politzer (Eds.), *Modern Density Functional Theory: A Tool for Chemistry* (Elsevier, Amsterdam, 1995) p. 349.
- [20] M. Harada and H. Dexpert, *J. Phys. Chem.* 100 (1996) 565.
- [21] A. Goursot, I. Papai and D.R. Salahub, *J. Am. Chem. Soc.* 114 (1992) 7452; A. Goursot, I. Papai and C. Daul, *Int. J. Quantum Chem.* 52 (1994) 799.
- [22] P.E.M. Siegbahn, M.R.A. Blomberg and M. Svensson, *J. Phys. Chem.* 98 (1994) 2062; M.R.A. Blomberg, P.E.M. Siegbahn and M. Svensson, *J. Am. Chem. Soc.* 114 (1992) 6095.
- [23] B. Delley, *Chem. Phys. Lett.* 110 (1986) 329.