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Acetylene trimerization on Ag, Pd and Rh atoms deposited on MgO thin films

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The acetylene trimerization on the group VIII transition metal atoms, Rh and Pd, as well as on Ag atoms supported on MgO thin films has been studied experimentally and theoretically. The three metal atoms with the atomic configurations $4d^85s^1$ (Rh), $4d^{10}s^0$ (Pd) and $4d^{10}5s^1$ (Ag) behave distinctly differently. The coinage metal atom silver is basically inert for this reaction, whereas Pd is active at 220 and 320 K, and Rh produces benzene in a rather broad temperature range from 350 to *ca.* 430 K. The origins of these differences are not only the different electronic configurations, leading to a weak interaction of acetylene with silver due to strong Pauli repulsion with the 5s electron but also the different stability and dynamics of the three atoms on the MgO surface. In particular, Rh and Pd atoms interact differently with surface defects like the oxygen vacancies (F centers) and the step edges. Pd atoms migrate already at low temperature exclusively to F centers where the cyclotrimerization is efficiently promoted. The Rh atoms on the other hand are not only trapped on F centers but also at step edges up to about 300 K. Interestingly, only Rh atoms on F centers catalyze the trimerization reaction whereas they are turned inert on the step edges due to strong steric effects.

1. Introduction

The cyclotrimerization of acetylene to form benzene, $3C_2H_2 \rightarrow C_6H_6$, is a well-known reaction studied on single crystal surfaces from UHV conditions $(10^{-12}-10^{-8} \text{ atm})$ to atmospheric pressure $(10^{-1}-1 \text{ atm})$.¹⁻⁴ On the Pd(111) surface^{5.6} the reaction proceeds through the formation of the intermediate, C_4H_4 ,⁷⁻¹⁰ to which an additional acetylene molecule is bound to form benzene. The entire process can be divided into three steps:¹¹

$$Pd_{site} + 2C_2H_2 \rightarrow Pd_{site}(C_2H_2)_2 \rightarrow Pd_{site}(C_4H_4)$$
 (1)

 $Pd_{site}(C_4H_4) + C_2H_2 \rightarrow Pd_{site}(C_4H_4)(C_2H_2)$

$$\cdot \operatorname{Pd}_{\operatorname{site}}(\operatorname{C}_6\operatorname{H}_6) \tag{2}$$

$$Pd_{site}(C_6H_6) \rightarrow Pd_{site} + C_6H_6$$
 (3)

On Pd(111) the first two steps, reactions (1) and (2), occur with very low energy barriers whereas the desorption of benzene (3) is the rate determining step. For low benzene coverages, formation of benzene is observed at around 500 K. This reaction has also been studied on size-selected Pd_n clusters deposited on MgO thin films grown on a Mo(100) surface.¹² The cluster-assembled materials obtained in this way exhibit peculiar activity and selectivity in the polymerization of acetylene to form benzene and aliphatic hydrocarbons.¹³ Up to Pd₃ only C₆H₆ is formed, whereas the branching ratio for the formation of C_6H_6 , C_4H_6 and C_4H_8 varies with size for larger clusters. Theoretical calculations¹⁴ have shown that for isolated atoms the reaction mechanism is the same as for the Pd(111) surface and that the interaction with the substrate is essential in activating the Pd atom for this reaction. In fact, a free Pd atom is inert for the cyclotrimerization reaction and the activation is connected to the existence of donor levels on

the surface of the oxide. The theoretical results suggest that the oxygen vacancies at the surface of MgO (so called F centers) are responsible for the stabilization of the Pd atoms, and for the enhancement of their reactivity *via* charge transfer. An additional proof of the active role of F centers originates from the analysis of the adsorption of CO on Rh, Pd and Ag atoms deposited on a MgO thin film: Fourier transform infrared (FTIR) and temperature programmed desorption (TPD) spectra in combination with *ab initio* calculations indicate that the F centers are most likely the trapping sites for these metal atoms. In addition, these studies revealed complex diffusion patterns of both the metal atoms and the metal–CO complexes on the MgO surface when the substrate temperature is increased.

Despite the detailed picture accumulated so far, there are still several open questions, e.g. whether F centers play a similar role for other metal atoms or how the element-specific stabilities of metal atoms on the oxide surface are manifested in their chemical reactivities. A way to gain insight into these problems is to investigate systematically a series of deposited transition metal atoms. Here we present a comparative study of the acetylene cyclotrimerization on Ag, Pd and Rh atoms. Such a comparison is interesting as the electron configuration changes from $4d^85s^1$ of Rh to $4d^{10}5s^0$ for Pd and to $4d^{10}5s^1$ for Ag. The interplay between s and d occupation in the three metals is relevant for both the analysis of the interaction with the donor levels of the substrate, and for studying the activation of the adsorbed molecules. The cyclotrimerization of acetylene on Ag1/MgO, Pd1/MgO and Rh1/MgO has been studied experimentally by means of temperature programmed reaction (TPR) spectroscopy in combination with DFT calculations to get information on the reaction mechanism. The obtained results show that, in contrast to Pd and Rh atoms, Ag is inert independently of the adsorption site. In addition, both

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Pd and Rh atoms are only reactive when stabilized at F centers. However, while diffusion processes do not seem to play an important role in the activity of supported Pd atoms, they have a major effect on the chemistry of supported Rh atoms.

2. Experimental and computational details

2a. Experiments

The metal atoms are produced by a high-frequency laser evaporation source.¹⁵ The positively charged ions are guided by home-built ion optics through differentially pumped vacuum chambers and are size-selected from the cluster distribution by a quadrupole mass spectrometer (Extrel Merlin System; mass limits: 1000, 4000, 9000 amu) before deposition onto thin MgO(100) surfaces with a known density of F centers.

In these films the oxygen vacancies are generated by using a defined preparation procedure (Mg evaporation rate: 2–5 ML min⁻¹, O_2 background: 10^{-6} Torr).¹⁶ The films are then annealed to 840 K for 10 min. Auger electron spectroscopy (AES) measurements show a one-to-one stoichiometry for magnesium and oxygen and the absence of any impurity.¹⁵ When not indicated elsewhere the thicknesses are about 10 monolayers, as determined by AES peak intensities and by X-ray photoemission (XPS), using the intensity attenuation of the Mo 3d core level with increasing film coverage.¹⁷ The films have also been studied by electron energy loss spectroscopy¹⁸ and exhibit characteristic losses between 1 and 4 eV, lying within the MgO band gap. Similar loss structures have been observed before¹⁹ and according to first-principle calculations using large cluster models, they have been attributed to transitions, characteristic for neutral surface F centers in various coordinations on flat terraces, at steps and at kinks.²⁰ The density of these oxygen vacancies is estimated to be larger than $5 \times 10^{13} \text{ cm}^{-2}$.

In these experiments it is important to deposit 0.5-0.8% of a monolayer atoms (1 ML = 2.25×10^{15} clusters cm⁻²) only at 90 K and with low kinetic energy in order to land them isolated on the surface and to prevent agglomeration on the MgO films. Monte Carlo simulations revealed that under such experimental conditions, *e.g.* cluster flux (*ca.* 10^9 cm⁻¹), cluster density (*ca.* 10^{13} cm⁻¹), and defect density (*ca.* 5×10^{13} cm⁻¹) on the MgO(100) films, less than 10% of the atoms coalesce during migration to the trapping centers.²¹

The chemical reactivity and stability of the deposited metal atoms is studied by TPD and by FTIR studies. The latter is mainly used to investigate the stability of the atoms on the surface by using the probe molecule CO.

2b. Calculations

For the calculations we have used the same embedded cluster approach adopted to model reactions (1) and (2) on Pd_1/MgO . The sites considered for adsorption are: terrace O_{5c}^{2-} , step ${O_{4c}}^{2-},\ F$ and F^+ centers at a terrace and they have been represented by the following clusters: O9Mg5 for terrace, $O_{12}Mg_{10}$ and $O_{15}Mg_{12}$ for step, O_8Mg_5 for neutral F_s and $[O_8Mg_5]^+$ for the positively charged F_s^+ center. The MgO clusters have been embedded in effective core potentials (ECP) and a large array of point charges (PC) in order to represent the Madelung potential in the cluster region.²² The whole system, cluster + ECPs + PCs is electrically neutral, except for the F_s^+ center which carries a net positive charge. The positions of the adsorbed molecules, of Rh or Ag atoms and of their first neighbors on the MgO surface have been fully optimized with no symmetry constraints. The transition state (TS) search for reactions (1) and (2) has been performed using the Berny algorithm and in selected cases the nature of the TS has been verified by performing a frequency analysis. The calculations have been performed in spin polarized mode. All Ag and Rh surface complexes have doublet ground states with

the only exception of complexes formed on F_s^+ centers where the ground state is singlet.

Gaussian-type atomic orbital basis sets were employed to construct the Kohn–Sham orbitals. The 6-31G* basis set has been used for O and Mg.²³ In the F_s^+ and F_s cases where one or two electrons, respectively, are trapped in the vacancy, a diffuse 6-31+G* basis set has been employed on the Mg atoms nearest the vacancy to describe the electron localization in the cavity.²⁴ A 18-electrons ECP where the 4s²4p⁶4d¹⁰ electrons are explicitly treated in the valence, and a double- ζ plus polarization basis have been used for Rh and Ag (LanL2DZ),²⁵ while C and H have been treated with a 6-311G(p,d) basis. No basis set superposition error (BSSE) correction has been applied to the results. The calculations have been performed at the spin-polarized DFT level with the B3LYP functional.^{26,27} All calculations have been performed with the GAUSSIAN98²⁸ package.

3. Results

3a. Experiments

To characterize the model catalysts in more detail, it is necessary to identify experimentally the adsorption sites of the clusters in order to relate the results to the computational investigations. We first summarize results published elsewhere,²⁹ where the probe molecule CO is used to get information on the stability and dynamics of the adsorbed atoms. As an example, CO desorbs from the adsorbed Pd atoms at a temperature of about 250 K,³⁰ which corresponds to a binding energy, $E_{\rm b}$, of about 0.7 \pm 0.1 eV. FTIR spectra suggest that at saturation two different sites for CO adsorption exist on a single Pd atom. The vibrational frequency of the most stable, singly adsorbed CO molecule is 2055 cm⁻¹. Density functional cluster model calculations have been used to model possible defect sites at the MgO surface where the Pd atoms are likely to be adsorbed. CO/Pd complexes located at regular or lowcoordinated O anions of the surface exhibit considerably stronger binding energies, $E_b = 2-2.5$ eV, and larger vibrational shifts than were observed in the experiment. CO/Pd complexes located at oxygen vacancies (F or F⁺ centers) are characterized by much smaller binding energies, $E_{\rm b} = 0.5 \pm 0.2$ or 0.7 ± 0.2 eV, which are in agreement with the experimental value. This comparison not only identifies adsorption sites of the atoms on the MgO surface, but by the absence of vibrational frequencies typical for bridge-bonded CO (up to about 300 K) it is concluded that the atoms stay well-isolated. The thermal stability was also investigated for Rh atoms and it was found that they are stable up to at least 450 K.²

For the cyclotrimerization on deposited Ag, Pd and Rh atoms, the nanocatalysts were exposed at 90 K, using a calibrated molecular beam doser, to about 1 Langmuir (L) of acetylene. In a TPR study, catalytically formed benzene (C_6H_6), butadiene (C_4H_6) and butene (C_4H_8) were monitored by a mass spectrometer as function of temperature. It is interesting to note that the reactant (C_2H_2) is only physisorbed on MgO and desorbs at temperatures lower than 150 K, *e.g.* before the reaction takes place.

Fig. 1 depicts the results for Rh atoms. Clearly, only the cyclization of C_2H_2 is catalyzed by the Rh atoms and other possible products like H_2 , C_4H_4 , C_4H_6 or C_4H_8 are not formed, thus Rh atoms are very selective for the cyclotrimerization reaction. The formation of C_6H_6 occurs in a rather broad temperature window between 375 and 475 K. In contrast to Pd atoms the reaction temperature is distinctly higher for Rh. Earlier studies revealed that, depending on the thickness of the defect-rich MgO films, benzene is formed on Pd atoms at 220 K (Fig. 2a) or 300 K (Fig. 2b), respectively. This change in temperature was not observed for the other two metals (Rh and Ag) and the origin of this observation is not yet clear.



Fig. 1 TPR spectra of the catalytic formation of C_6H_6 (a) and C_4H_4 , C_4H_6 , C_4H_8 and C_6H_{12} (b) on deposited Rh atoms. The atom density on the thin MgO films was 0.8% ML (1 ML = $2.2 \times 10^{15} \times cm^{-1}$) and the model catalysts were exposed at 90 K to 1 Langmuir (L) of acetylene. Rh atoms selectively form benzene in a rather broad temperature range starting from around 300 K up to about 550 K.

Another difference with respect to Rh are the much narrower C_6H_6 desorption peaks for Pd atoms, for the low-temperature formation the width is just 25 K (Fig. 2a). As in the case of rhodium, Pd atoms are very selective for the formation of benzene at both temperatures. The behavior of Ag-atoms is completely different and none of the possible product molecules (H₂, C₄H₄, C₄H₆, C₄H₈, C₆H₆) were detected as shown in Fig. 3.

3b. Calculations

Ag₁/MgO. Ag atoms deposited on the terrace sites do not bind C_2H_2 . The geometry optimizations show the existence of a local minimum 0.44 eV above the dissociation limit; this is in line with the results for CO adsorption on Ag₁/MgO, which show little or no tendency of the supported Ag atoms to adsorb molecules. When the Ag atoms are trapped at the F centers the acetylene molecules are only slightly bound (0.07 eV); as these results have not been corrected by the BSSE we conclude that for none of the defect sites considered in this work Ag atoms bind acetylene. These results are consistent with the experimental observation that Ag is inert towards the formation of benzene. The inert character of Ag must be related to the presence of a partially occupied 5s level. This orbital is spatially expanded and since the 5s electron cannot be promoted into the filled 4d shell (unlike for Rh or Pd) a strong Pauli repulsion occurs. The only way to increase the Ag activity would be the oxidation of the atom to reduce the population of the 5s orbital; this process is however not possible on a basic oxide like MgO.



Fig. 2 TPR spectra of the catalytic formation of C_6H_6 on deposited Pd atoms. The atom density on the thin MgO films was 0.8% ML (1 ML = 2.2×10^{15} cm⁻¹) and the model catalysts were exposed at 90 K to 1 Langmuir (L) of acetylene. Depending on the preparation method of the defect-rich films a reaction temperature at 220 K (a) and 320 K (b) was observed. Note that the peaks of the C_6H_6 formation are narrow (fwhm: *ca.* 15 K (a); *ca.* 40 K (b)) in comparison to Rh atoms. In none of the experiments could both peaks be detected in the same spectrum. This behavior was only observed in the case of Pd atoms. The origin of the temperature change is not yet understood.

Free Rh atoms. Before considering the activity of supported Rh atoms, we discuss the cyclotrimerization reaction on a free Rh atom (Figs. 4 and 5). Rh binds acetylene by 1.57 eV and the ground state is doublet (Figs. 4a and 5); the adsorption is accompanied by a substantial activation of the molecule (elongation of the C-C bond, loss of linearity (Table 1)). The second acetylene is adsorbed with an energy gain of 1.23 eV to give rise to the complex shown in Fig. 4b. A very small barrier, 0.04 eV, separates this structure from the $Rh(C_4H_4)$ complex (Fig. 4c) a stable intermediate which is 0.86 eV lower in energy than $Rh(C_2H_2)_2$. $Rh(C_4H_4)$ can adsorb a third acetylene molecule with a gain of 0.76 eV to form $Rh(C_4H_4)(C_2H_2)$ (Fig. 4e). This is the precursor state of the final product, $Rh(C_6H_6)$ (Fig. 4f), from which it is separated by a barrier of 0.24 eV (Fig. 5). The last step is associated with an energy gain of 2.10 eV (Fig. 5). Once formed, benzene is immediately released as it is virtually unbound to the metal atom (Fig. 5). Thus, on a free Rh atom the reaction occurs with very small barriers. Notice that Rh is able to bind even three acetylene molecules; $Rh(C_2H_2)_3$ (Fig. 4d), is more stable than $Rh(C_2H_2)_2 +$ C₂H₂ by 0.5 eV. In this respect, Rh has quite a distinct behavior compared to Pd. In fact, a gas-phase Pd atom binds only weakly the third acetylene and is thus inert for the reaction.12,14 The fact that benzene is formed on Pd atoms



Fig. 3 TPR spectra of the catalytic formation of C_6H_6 (a) and C_4H_4 , C_4H_6 , C_4H_8 and C_6H_{12} (b) on deposited Ag atoms. The atom density on the thin MgO films was 0.8% ML (1 ML = 2.2×10^{15} cm⁻¹) and the model catalysts were exposed at 90 K to 1 Langmuir (L) of acetylene. In contrast to Pd and Rh atoms, only a very small amount of C_6H_6 is formed on Ag atoms.

supported on MgO reveals the active role of the substrate in contrast to Rh.

 Rh_1/MgO (terrace). Previous work has shown that Rh atoms have a high mobility on the MgO surface. The diffusion barriers, E_d , from an O_{5c} site to the next one are of the order of 0.1 eV. Using an Arrhenius expression from transition state



Fig. 4 Structure of gas-phase Rh–acetylene complexes: (a) Rh(C_2H_2); (b) Rh(C_2H_2); (c) Rh(C_4H_4); (d) Rh(C_2H_2); (e) Rh(C_4H_4)(C_2H_2); (f) Rh(C_6H_6).



Fig. 5 Energy profile for the conversion of acetylene to benzene promoted by a gas-phase Rh atom. In the insets are shown the structures of the two transition states involved in the reaction mechanism.

theory $\Gamma \approx \Gamma_0 \exp(-E_{\rm d}/kT)^{31}$ and a pre-exponential factor $\Gamma_0 = 10^{13}$ Hz, one can estimate, at a deposition temperature of 100 K, a hopping frequency $\Gamma \approx 89$ GHz and a residence time $\tau = 1/\Gamma \approx 1.1 \times 10^{-8}$ s. As a consequence, the kinetic energy of atoms arriving on the surface and the thermal energy of the substrate are sufficient to induce extremely rapid diffusion on the flat terraces even at low temperature; the diffusion process will stop only in the presence of strong binding sites like steps or oxygen vacancies (F or F⁺ centers). Thus, it is very unlikely that Rh atoms deposited on the (100) faces will be involved in the trimerization reaction. Still, reactions (1)-(3) have been considered on this site for the sake of completeness. A Rh atom bound to a MgO terrace binds the first (Fig. 6a) and second (Fig. 6b) acetylene molecule strongly, $D_{e1} = 2.23$ eV and $D_{e2} =$ 0.89 eV, respectively (Fig. 7); the formation of the C_4H_4 intermediate (Fig. 6c) is exothermic, $\Delta E = -0.83$ eV and acetylene binds also to the Rh(C₄H₄) complex ($D_{e3} = 0.90$ eV, Fig. 6d). However, the barrier for the first transition state, $Rh(C_2H_2)_2 \rightarrow Rh(C_4H_4), \Delta E_1^{\#} = +1.74 \text{ eV}$, is quite high (Fig. 7). The second barrier, $Rh(C_4H_4)(C_2H_2) \rightarrow Rh(C_6H_6), \Delta E_2^{\#} =$ 0.40 eV, is much smaller, indicating that step (1) is rate determining. Once formed, benzene is bound to the supported Rh atom by 0.92 eV (Figs. 6e and 7).

Unlike the gas phase, the supported $Rh(C_2H_2)_3$ complex is unstable and tends to dissociate one of the three acetylene molecules. The reason may be steric hindrance. In fact, in the free $Rh(C_2H_2)_3$ complex one acetylene is normal to the plane containing the Rh atom and the other two acetylene molecules; on the surface this arrangement is not possible because of the repulsive interaction with the substrate. In general, steric hindrance has an important consequence for the whole reactivity. The propensity of the Rh atom to promote the trimerization reaction is in fact strongly reduced on the MgO support. The strongest manifestation of this effect is the high barrier to transforming two adsorbed acetylene molecules into a C_4H_4 intermediate. The barrier, 1.74 eV, exceeds the binding energy of acetylene. One reason for this large activation barrier is the attractive interaction of the two

Table 1 Adsorption properties of $C_2 H_2$ on free Rh atom and on Rh/MgO complexes

		Rh on MgO			
	Free Rh	O _{terrace}	O _{step}	F	\mathbf{F}^+
d(C-C)/Å	1.288	1.278	1.315	1.274	1.247
d(C-Rh)/Å	1.977	2.004	1.960	2.052	2.135
∠(H–C–C)/°	147.9	149.8	140.2	149.6	157.4
$D_{\rm e}({\rm C_2H_2})/{\rm eV}$	1.57	2.23	1.76	1.06	0.58
$D_{\rm e}({\rm RhC_2H_2})/{\rm eV}$	—	1.65	2.50	2.82	1.76



1.943 Å

MgO(001) terrace: (a) $Rh(C_2H_2)$; (b) $Rh(\hat{C_2H_2})_2$; (c) $Rh(C_4H_4)$; (d) $Rh(C_4H_4)(C_2H_2)$; (e) $Rh(C_6H_6)$. Selected distances are given.

acetylene molecules with the surface (Fig. 6b). The H atoms of the two molecules form a kind of H-bonding with the surface oxide anions. The energy required to bring the two molecules together is thus much higher than in the gas phase.

Rh₁/MgO(step). At variance with Pd, Rh atoms bind quite strongly at step sites of the MgO surface $(D_e = 1.95 \text{ eV}).^{29}$ Thus, while these sites are of little interest in the case of Pd, they are potentially involved in the reactivity of Rh. The interaction of acetylene with a Rh atom at a step site has been analyzed in detail. At step sites Rh binds strongly the first acetylene, $D_{e1} = 1.77$ eV, see Fig. 8a. Among the cases



Fig. 7 Energy profile for the conversion of acetylene to benzene promoted by a Rh atom supported on a MgO(001) terrace. In the insets are shown the structures of the two transition states involved in the reaction mechanism.



Fig. 8 Structure of Rh-acetylene complexes supported on a MgO (001) step: (a) Rh(C₂H₂); (b) Rh(C₂H₂)₂. Selected distances are given.

considered in this work, this site corresponds to the strongest activation of acetylene, as shown by the long C-C distance, short C-Rh distance, and small HCC angle (Table 1). The $Rh(C_2H_2)$ complex is bound to the surface by 2.5 eV, with the Rh atom interacting simultaneously with the O4c atom of the step, r(O-Rh) = 2.168 A, and with the O_{5c} anion of the basal plane, r(O-Rh) = 2.386 Å (Fig. 8a). The larger activation of the acetylene molecule reflects the interaction with two surface basic sites. The high stability of the $Rh(C_2H_2)$ complex makes it difficult to bind the second acetylene molecule: various geometries have been considered but we find only unbound or weakly bound $Rh(C_2H_2)_2$ complexes (Fig. 8b) (the calculations have been repeated with the larger $O_{15}Mg_{12}$ cluster but the results do not change). Again, this is due in part to steric effects, since Rh cannot easily accommodate two acetylene molecules when it is bound at a step.

Based on these results and assuming that Rh atoms are bound at the MgO step sites, one cannot explain the observed trimerization of benzene. On the other hand, $Rh(C_2H_2)$ complexes form easily at these sites. The barrier for diffusion of $Rh(C_2H_2)$ from a step to a terrace site is <1.4 eV, *i.e.* smaller that the energy required to detach acetylene. This means that a temperature increase may result in the diffusion of the $Rh(C_2H_2)$ complex before acetylene desorption occurs.

Rh₁/MgO(F center). As other metal atoms, also Rh binds strongly at F centers. This surface complex binds C₂H₂ by 1.06 eV (Table 1). It is interesting to note that the properties of the adsorbed hydrocarbon molecule on Rh/F_{5c} are similar to those computed for Rh on a terrace site (Table 1 and Fig. 9). The main difference however is in the binding energy: on the F center it is about one-half that on the terrace. Rh/F_{5c} can bind a second C_2H_2 molecule by 0.96 eV. The formation of the C_4H_4 complex implies an energy gain, $\Delta E = -0.91$ eV (Fig. 10) similar to that observed for Rh on step and terrace sites and even in the gas phase. A third acetylene can be added to the $Rh(C_4H_4)$ complex on a F center with $D_{e3} = 0.90$ eV (Fig. 9d). The formation of benzene is exothermic by 3.23 eV, and the resulting molecule (Fig. 9e) is only weakly bound to the supported atom ($D_e = 0.40$ eV). The barriers for steps (1) and (2) of the reaction are similar, $\Delta E_1^{\#} = +1.18$ eV, $\Delta E_2^{\#} =$ +1.07 eV (Fig. 10), and are about 20% higher than those computed for Pd. Frequency calculations of the saddle point structures show the existence of only one negative frequency value associated to the vibrational mode of the reaction coordination chosen for the reaction path. Thus, the two structures correspond to real TS's. If one assumes a Redhead equation and a 1013 pre-exponential factor, the computed barriers correspond to a desorption temperature of about 400 K. This temperature is comparable to the temperature of maximal benzene formation of 430 K, as observed in Fig. 1. Thus, Rh atoms trapped on F centers contribute to the formation of benzene at ca. 400 K. The quite broad peak observed experimentally which starts already at around 350 K, is due to the fact that some benzene can be formed during the diffusion of Rh-acetylene species on the terrace sites (e.g. by



Fig. 9 Structure of Rh–acetylene complexes supported on a neutral oxygen vacancy (F center) on the MgO(001) surface: (a) $Rh(C_2H_2)$; (b) $Rh(C_2H_2)_2$; (c) $Rh(C_4H_4)$; (d) $Rh(C_4H_4)(C_2H_2)$; (e) $Rh(C_6H_6)$.

formation of small Rh clusters). The fact that the barriers for benzene formation for Rh on F centers are about 20% higher than those computed for Pd on the same site¹⁴ is qualitatively consistent with the higher reaction temperature for the former atom (see Figs. 1 and 2).

Rh₁/MgO(F⁺ center). Rh on a F⁺ center is able to coordinate and activate two acetylene molecules; the first (Fig. 11a), is bound by 0.58 eV only, the second slightly more, 0.66 eV (Fig. 11b). The weak interaction of Rh/F_{5c}⁺ with acetylene is reflected in long C–C and Rh–C bonds, as well as in a large HCC angle (Table 1), typical signs for modest activation. On a F⁺ site the Rh(C₄H₄) complex (Fig. 11c), is 0.84 eV more stable



Fig. 10 Energy profile for the conversion of acetylene to benzene promoted by a Rh atom supported on a neutral F center on the MgO(001) surface. In the insets are shown the structures of the two transition states involved in the reaction mechanism.



Fig. 11 Structure of Rh–acetylene complexes supported on a charged oxygen vacancy (F^+ center) on the MgO(001) surface: (a) Rh(C₂H₂); (b) Rh(C₂H₂); (c) Rh(C₄H₄); (d) Rh(C₄H₄)(C₂H₂); (e) Rh(C₆H₆).

than Rh(C₂H₂)₂. The addition of the third acetylene molecule to Rh(C₄H₄) (Fig. 11d), occurs with a gain of 1.01 eV. Thus, all the intermediates have a sufficiently high stability for the reaction to occur according to steps (1)–(3). From the Rh(C₄H₄)(C₂H₂) complex one can form benzene with a large gain of 3.79 eV (Fig. 12). As for the neutral F center, benzene is weakly bound to the supported Rh atom and immediately desorbs ($D_e = 0.24$ eV). Despite several attempts, the search for the transition states of steps (1) and (2) has failed. Only rough estimates have been obtained. A scan of the potential energy surface for step (1) suggests a barrier <0.7 eV. For step (2) even the scan of the potential energy surface has not produced stable results, and no estimate of the barrier has been obtained.



Fig. 12 Energy profile for the conversion of acetylene to benzene promoted by a Rh atom supported on a charged F^+ center on the MgO(001) surface. In this case it has not been possible to identify the transition states (see text).

Therefore, evidence about the ability of the F^+ center to promote the trimerization reaction is only partial, and based exclusively on the stability of the various intermediates.

4. Discussion and conclusions

In this section we formulate a plausible hypothesis for the observed different behavior in the trimerization of acetylene promoted by Rh, Pd and Ag atoms deposited on MgO thin films on the basis of the findings described above. Ag is practically inert for this reaction, as found both experimentally and theoretically. This low reactivity is due to the Pauli repulsion between the valence 5s electron on Ag and the incoming molecules. This repulsive interaction does not allow the acetylene molecules to bind to the metal atom, so that no further reaction is possible. Interestingly, larger Ag clusters are not catalyzing this reaction either.

The Pd case has been studied in detail in the past.¹²⁻¹⁴ It was found that the reaction on Pd₁/MgO can be explained only by assuming that the oxygen vacancies, either in neutral or charged forms, are directly involved. The general picture is that Pd atoms are deposited at low temperature (<100 K) on the MgO thin films and that they possess enough residual kinetic energy once they land on the surface to freely diffuse; in fact, the thermal energy of the substrate only is not sufficient to overcome the diffusion barrier, $E_{\rm d} \approx 0.4 \, {\rm eV.}^{32}$ In the diffusion process the Pd atoms are likely to be trapped at specific sites where the interaction is stronger. Among these are point defects like oxygen vacancies, divacancies but not extended defects as steps. In fact, Pd atoms bind at steps with an adsorption energy only slightly higher than on flat terraces.²⁹ As a consequence, the trapping energy for a Pd atom on a step is relatively small and the Pd atoms most likely populate the F centers present on the surface before acetylene is introduced in the reaction chamber. This would explain the narrow peak observed in the TDS spectrum of Fig. 2a assuming all the active atoms to reside on the same site. From this point of view the picture is relatively simple, and the only open question is related to the nature of the trapping site, F, F⁺, or other sites not considered so far (e.g., divacancies). The best candidates are the F and the F^+ centers because (a) they are both strong trapping sites for Pd atoms, and (b) the energy profile for the reaction occurring on these centers are to a large extent consistent with the measured desorption temperature (the reaction profiles for Pd on other MgO sites are totally inconsistent with the experiment). In comparison to larger clusters, single atoms are very selective for the formation of benzene. In fact, by increasing cluster size the branching ratio of possible product molecules is changing in favor of C₄H₆ for cluster sizes with around 8 atoms and in favor of C₆H₈ for sizes around 30 atoms.¹³

The situation for Rh is far more complex. Recent combined experimental and theoretical studies based on the use of CO as a probe molecule have shown that Rh atoms are more mobile than Pd atoms on MgO.²⁹ The barrier for diffusion of Rh on the flat terraces is about one third that of Pd. However, at variance with Pd, Rh atoms bind quite strongly at the step sites (the binding energy on these sites is about twice that on the terrace sites).²⁹ The work done on $CO/Rh_1/MgO$ suggests that a significant fraction of the Rh atoms are bound at steps already at low temperature and that only a minority of the deposited Rh atoms have been stabilized at F centers in the diffusion process (this can be explained with the higher probability to encounter an extended defect like a step than a point defect like an F center in the diffusion process). Thus, Rh atoms at steps could be involved in the cyclization reaction. However, the calculations show that by exposure to acetylene one can form a stable $Rh(C_2H_2)$ complex but not the $Rh(C_2H_2)_2$ or $Rh(C_2H_2)_3$ complexes, which are essential to promote the reaction. Steric effects reduce the binding ability

of the Rh atom supported at a step and rule out this surface complex as a potential catalyst for the reaction. The binding of acetylene to Rh supported on a MgO step, 1.77 eV, is such that only at high temperature acetylene will desorb from this site. Thus, as temperature increases it is more likely to induce diffusion of the stable Rh(C2H2) unit rather than acetylene dissociation. A very similar conclusion has been drawn for the case of CO adsorption.²⁹ Indeed, we evaluate that the barrier to displace $Rh(C_2H_2)$ from a step to a terrace site is about 1.3 eV. This means that around room temperature two different processes can occur. If the Rh atoms have been directly stabilized at the F centers (minority sites) the reaction will take place on these sites as it has been found for Pd. In the case where the Rh atoms are trapped at step sites, the $Rh(C_2H_2)$ complexes start to detach from the steps, diffuse on the surface until they are captured by an empty F center. $Rh(C_2H_2)$ binds by 2.8 eV or 1.77 eV to F or F⁺ centers, respectively. On these new sites the reaction can occur only if additional acetylene molecules are readsorbed from the gas phase or by reverse spill-over from the surface. The latter, however, is unlikely when considering the relative low binding energy of acetylene on pure MgO. The other possibility is that the Rh(C₂H₂) unit diffuses until it encounters another Rh or $Rh(C_2H_2)_n$ complex stabilized at a nucleation center (F center, divacancy, etc.). This would lead to the nucleation of a small cluster and benzene could form from this new species. The existence of a complex diffusion pattern induced by the temperature increase can explain the broad peak observed in the TPD spectrum. According to the proposed explanation, benzene could form in part from isolated Rh atoms at F centers and in larger part from very small clusters generated during the adsorbate-induced diffusion. In this respect it is important to note that larger clusters (Rh₁₀-Rh₃₀) do not show any reactivity for the polymerization of acetylene.

In summary, the specific electronic configuration of silver renders these atoms inert for the polymerization of acetylene. Pd atoms, on the other hand, are turned into active catalysts for the cyclotrimerization reaction only when adsorbed on color centers as charge is donated from this defect site into the atom. Finally, although already reactive as free atoms, Rh atoms on a MgO surface catalyze the cyclotrimerization only when trapped on F centers as otherwise steric effects reduce the stability of the intermediates.

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