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Theoretical studies of CO adsorption and dissociation on Ru in presence of Cl or MoO_x

A. Juan [b], D.E. Damiani [a,1] and N.J. Castellani [a,b]

[a] *PLAPIQUI (UNS–CONICET), 12 de Octubre 1842, 8000 Bahía Blanca, Argentina*
[b] *Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253,*
8000 Bahía Blanca, Argentina

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Using the extended Hückel molecular orbital method we studied the adsorption and dissociation of CO over a Ru cluster with Cl or MoO preadsorbed onto it. Previous experimental information oriented us to think that the remaining Cl present in Ru/SiO_2 and $RuMo/SiO_2$ catalysts could influence their chemisorptive and catalytic properties. On this basis our theoretical model explains the observed activity and selectivity during the CO + H_2 reaction, that is, Cl decreases the adsorption of CO and hinders its dissociation. This could lead to the appearance of methanol as a synthesis product. On the other hand, our theoretical calculations indicate that the presence of MoO on top of the Ru cluster favors the adsorption of CO parallel to the cluster surface. They also predict an energy barrier for its dissociation which is interpreted in terms of the possible insertion of this CO molecule into a metal–methyl bond thereby forming the ethanol precursor.

Keywords: CO dissociation; CO adsorption; theoretical study

1. Introduction

There is now considerable support for the idea that hydrocarbons are produced by dissociative adsorption of CO and subsequent hydrogenation of Cads. [1]. On the other hand the synthesis of methanol is believed to proceed by non-dissociative adsorption of CO [2]. For the formation of higher oxygenates, however, not only dissociative adsorption, but also associative adsorption of CO is of importance [3]. Depending on the reaction conditions the dissociative adsorption of CO may become rate-determining and this is of special interest [4]. In studies performed on several transition metal surfaces it has been shown that the adsorption of electronegative additives such as halogens or chalcogens inhibits the dissociation of CO,

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[1] To whom correspondence should be addressed.

and, on the other hand, the presence of alkaline promoters like K strongly enhances the dissociative adsorption of CO [5,6].

Although attention to the influence of impurities on CO adsorption has been devoted by several authors the theoretical study of CO dissociation is rather scarce [7]. Recently CO dissociation on a Rh (111) surface has been studied by de Koster and van Santen, showing that the lying-down CO is an activated species before the carbon and oxygen atom move to hollow sites on the Rh surface [8]. Similar calculations devoted to the Ru surface have not been found in the literature. However, Anderson et al. have studied the chemisorption of CO on Ru(001) (and K + Ru(001)) using a modified extended Hückel method [9].

In the present work we have examined the adsorption and dissociation of CO on the Ru(001) plane in the presence of other coadsorbates using the extended Hückel (EH) method. We modelled the catalytic systems CO + Cl/Ru and CO + MoO_x/Ru using a Ru metallic cluster on top of which CO dissociation takes place. The extended Hückel method is a suitable formalism to study electronic energy changes where transition metal atoms are involved. Moreover, the method is useful to obtain qualitative trends in order to make relative comparisons [10]. This theoretical approach (based on experimental information) to model well defined surface systems develops some principles that could be extrapolated to real systems. One of the disadvantages of the EH method is that a reliable geometry optimization is not possible. Therefore experimental data, if available, must be used for bond lengths and distances. The EH method is parameter dependent since the parameter selection determines the accuracy of the results and finally the absence of explicit electrostatic interactions poses another limitation. This is not so in the case of more sophisticated ab initio methods, although the EH method offers the advantage of computational economy and simplicity in the interpretation of its results. These advantages make possible the use of this method as a screening tool for better catalytic materials.

1.1. THEORETICAL METHOD AND CLUSTER MODELS

In this work the binding energy of CO species (E_{bCO}) to the Ru(001) cluster was calculated as the difference between the electronic energy of the system when the adsorbed CO molecule (dissociated or not) is at finite distance of the surface ($E_{(CO+Ru)}$), and the same energy when that molecule is far away from the solid ($E_{CO} + E_{Ru}$). In the calculations involving the presence of co-adsorbates, Ru is the Ru_{22} cluster with Cl or MoO on top of it.

The EH atomic parameters (see table 1) are taken from ref. [11] for C, O and Cl. In the case of Ru and Mo the parameters are taken from ref. [12]. The coefficients for the double expansion are from [13]. The ionization potentials are adopted from reported experimental data [14].

Table 1
Atomic orbital parameters

	n[a]		VSIP[b]	C_1[d]	ζ[c]	C_2[d]	ζ[c]
C	2	s	−16.59		1.625		
		p	−11.26		1.625		
O	2	s	−28.48		2.275		
		p	−13.62		2.275		
Cl	3	s	−24.54		2.033		
		p	−12.97		2.033		
Ru	5	s	−7.37		2.078		
		p	−4.11		1.743		
	4	d	−8.50	0.5340	5.378	0.6365	2.303
Mo	5	s	−7.10		1.96		
		p	−5.24		1.90		
	4	d	−8.50	0.6097	4.54	0.6097	1.900

[a] n: principal quantum number.
[b] VSIP: ionization potential (eV).
[c] ζ: Slater orbital exponent (a.u.).
[d] C_i: linear coefficients for double-zeta d-functions.

1.2. CO + Cl/Ru(001) MODEL

The (001) surface of Ru is represented by a 22 atom cluster, with two layers. The top one contains 14 atoms, the rest are in the bottom layer as shown in fig. 1. The Ru–Ru distance is that of the bulk crystal, that is 2.695 Å [15]. The same cluster model was used by Anderson et al. in the case of Pt(111) [16].

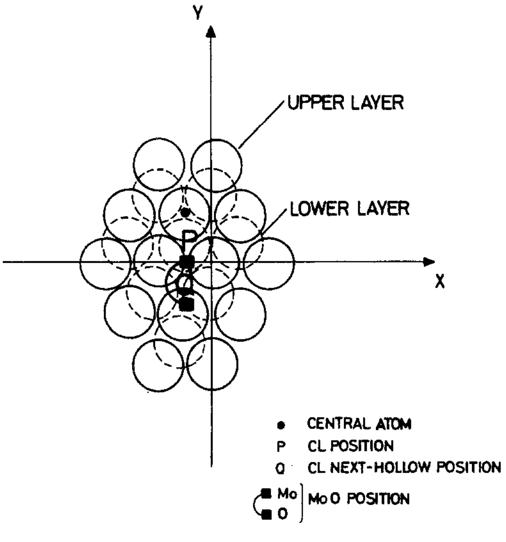

Fig. 1. Two-layer Ru_{22} cluster with Cl and MoO adsorption positions.

The place of the adsorption site is at or near the center of the cluster surface in order to minimize border effects. The CO molecule is adsorbed firstly in an end-on orientation with the C end towards the surface. High resolution EELS [17] and LEED [18] data suggest that CO is terminally bonded via the C atom to a single Ru atom and ESDIAD and EELS [19] measurements indicate that the majority of the CO is perpendicular to the macroscopic surface at all coverages. This monocoordinated position was named Top.

The transition state structure corresponding to the dissociation of the CO molecule is not known but it probably involves simultaneous interactions of C and O with two or more metal atoms. As the dissociation path is not completely elucidated, we have considered the idea of a progressive increase in the coordination of CO with the surface, through a model sequence of steps. For computational economy and as a first approach to the problem, we have performed the calculations for a not continuous sequence, implying four configurations of increasing coordination. In the first configuration, the CO molecule is adsorbed on top of a Ru atom. In the second one, the CO molecule is lying down between two Ru atoms. Following the terminology of Anderson, this is a Di-σ adsorbed CO. In the next configuration, named μ-π, the CO molecule is parallel to the Ru surface, with the C atom placed on a hollow site and the O atom on top of a Ru atom [9]. The final configuration corresponds to completely dissociated CO. As the isolated adatoms almost universally prefer the higher coordination sites on transition metal surfaces, we put both C and O atoms in hollow sites [20].

The selected geometries are given in fig. 2. The distances are shown in table 2.

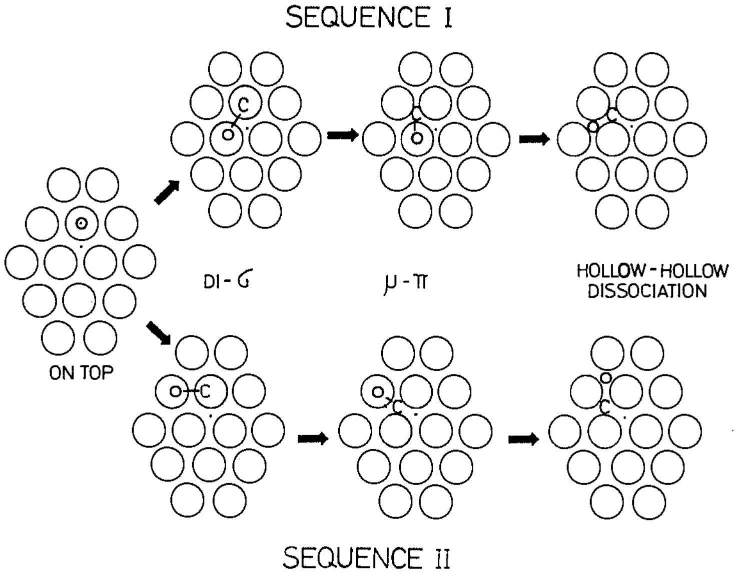

Fig.2. Sequences for CO dissociation.

Table 2
Distances used in the calculations (Å)

					Ref.
C–O	1.22				[9]
Ru–C	1.67				[30]
Ru–O	1.78				[30]
Ru–Cl	2.33				[30]
Mo–O	1.67				[22]
height Z(C)	1.80	(Di-σ)	1.60	(μ-π)	[9]
height Z(O)	1.80	(Di-σ)	1.60	(μ-π)	[9]
height Z(Mo)	1.90				[16]
height Z(O(Mo))	1.90				[16]
crystalline parameters of Ru(hcp)	$a = 2.695$	$c = 4.273$			[15]

The C–O, C–Ru and O–Ru distances are assumed equal to Anderson's reported values [9].

To study the effect of co-adsorbed Cl on CO dissociation we have considered two different sequences of steps. For both sequences, the Cl atom was placed on the nearest hollow site to CO Top (see fig. 1). In sequence I the Di-σ CO was also near the Cl but, in sequence II, it was in a next-neighbour position. The two final steps for both sequences have the C atom nearest to Cl. As it can be seen in fig. 2, the CO–Cl distance is larger for sequence II than for sequence I.

Finally we moved the Cl atom far away, to the next hollow site, to study the influence of CO–Cl distance on dissociation sequences I or II.

1.3. CO + MoO_x/Ru(001)

The Ru–Mo surface was modelled by means of the diatomic molecule MoO residing on the surface of the Ru(001) cluster. The choice of a diatomic molecule to represent the molybdenum oxide species is a simplifying approximation since the actual structures are not known. A great number of papers deal with the structure of Mo oxides on alumina but the same is not true for the case of Mo oxides on top of a metallic substrate.

Due to the lack of theoretical and experimental information we placed this molecule parallel to the Ru surface, in a two-fold site, like Anderson did for TiO/Pd or RuO/Ru systems [16,21]. The distance to the surface was not optimized because the extended Hückel method used did not include repulsive terms. It was fixed at 1.90 Å [16]. The Mo–O distance was taken to be the smallest from the MoO_3 bulk crystal (1.67 Å) [22].

The dissociation sequence was the same as for the CO + Cl/Ru(001) model.

2. Results and discussion

2.1. Cl-EFFECT ON CO DISSOCIATION

The binding energy of CO as a function of our discretized reaction coordinate is shown in fig. 3 for the clean Ru_{22} cluster. According to this, the parallel configurations Di-σ and μ-π of adsorbed CO are somewhat more stable than Top CO, as it was previously reported by Anderson et al. for the clean Ru surface [9]. When the CO molecule lies down there is a large overlap between CO and metal orbital. Since Ru does not have enough d-electrons to fully occupy the antibonding counterpart orbital, the donation from the occupied π orbital of CO is a stabilizing possibility (see fig. 2 in ref. [9] for example). In this way both the C and O atoms contact the surface and in this case π- and σ-donation and metal backbonding to the CO π^* orbital are all greater than in the case of Top CO.

It is also possible to observe the absence of an activation barrier in the considered CO dissociation sequence. This result is compatible with the well known property of Ru as a good methanation catalyst for which the C–O bond cleavage is considered fundamental [1], as we observed in Cl-free Ru/SiO_2 catalysts [23].

When the Cl atom is adjacent to CO Top we observe, in fig. 3, a noticeable increase in the system energy,adsorption becoming unfavorable by several eV. This negative influence on CO chemisorption agrees with the lower CO chemisorption values observed for chlorine-containing Ru/SiO_2 catalysts [23].

Theoretical studies of the poisoning and promotion in CO chemisorption have been presented in the framework of Blyholder's model, where the CO–metal surface bonding, for CO in an on top geometry, is a consequence of CO 5σ donation to the surface and a backdonation from the surface to the $2\pi^*$ levels of CO [24]. This electron transfer mechanism is geometrically compatible with a terminal carbon–

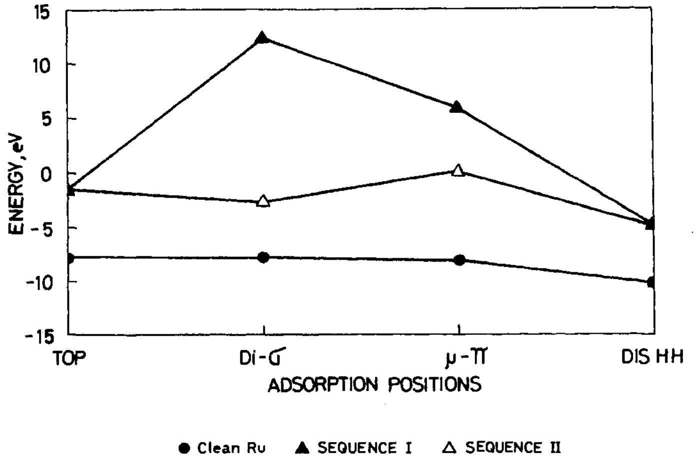

Fig.3. Binding energies for CO + Cl/Ru(001) (eV).

metal surface link, because both, 5σ and 2π* valence levels, are mainly centered on the carbon atom of the CO molecule [25]. Chlorine, sulfur and other electronegative atoms withdraw charge density from the surface, which lowers the backdonation and hence reinforces the C–O bond and weakens the C–metal bond [26]. The effect of electropositive atoms is just the opposite [9].

Sequences I and II show a great energy barrier for dissociation. This means that, if adsorbed, CO cannot proceed to Di-σ and/or μ-π configurations and remains in an on top position. This activation energy is lower for sequence II than for sequence I, where Cl and the CO molecule are closer. In a related work by Tomanek and Bennemann, the authors studied the dissociation of a CO molecule that falls parallel onto a Ni surface, represented by a four-atom cluster. Under the presence of Cl, as a substitutional impurity, the activation energy for CO dissociation increases, in the same way as in our results for Ru. However, the effect of Cl is much less important due to the fact that the pre-dissociated CO state is a down-lying CO and not a Top CO [7]. Experimental studies of CO adsorption on Ru(001) doped with Na show a tilt of this molecule toward the surface [27]. The electronegative nature of Cl could anticipate an opposite behavior, that is , in the presence of Cl the CO molecule tends to be perpendicular to the surface.

If we keep in mind that the mechanism proposed for methanol synthesis follows a non-dissociative route [1,2] the presence of residual Cl on Ru would justify the appearance of this oxygenated compound. Supported Ru catalysts containing Cl revealed methanol in the product distribution of the CO hydrogenation reaction, in agreement with the previous analysis [23].

In fig. 4 the binding energy–reaction coordinate relationship is plotted for the same sequences of fig. 3, when the Cl atom is moved to the next, more distant, hollow site. We observe that although the Top CO is not affected by the Cl atom, in

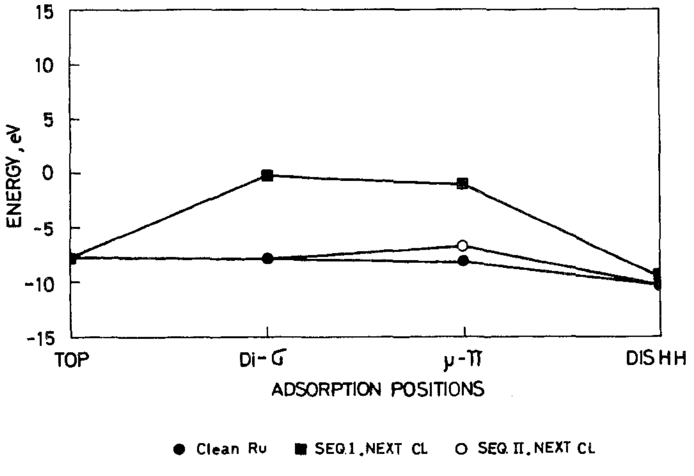

Fig.4. Binding energies for CO + Cl/Ru(001) with Cl in next hollow (eV).

sequence I an important activation energy is still present, while in sequence II there are no restrictions for the Di-σ configuration of the adsorbed CO molecule. Therefore, this interaction between Cl and CO seems to be localized and does not involve collective properties of the metal as suggested by the experimental results of Primet et al. and the theoretical results of Tomanek and Bennemann [7,31].

2.2. MoO EFFECT ON CO DISSOCIATION

In fig. 5 the binding energy of CO to the surface is plotted as a function of the reaction coordinate for the same dissociation sequences as in fig. 3 but now with a MoO species instead of an adsorbed Cl atom. Firstly we notice that MoO, contrary to Cl, yield more stable Top and Di-σ configurations for adsorbed CO molecules, in comparison to clean Ru. These theoretical results agree with our experimental finding of an increase in the desorption temperature of CO when Mo is incorporated onto supported Ru catalysts [23]. The effect is more pronounced for sequence I, when CO is closer to MoO. When the MoO species is moved to a more distant bridge site, its influence on CO dissociation is negligible. Moreover, both sequences I and II have a dissociation barrier of about 1 eV between the Di-σ configuration and the dissociated state. This barrier is much smaller than those corresponding to the Cl doped surface of fig. 3. As it is shown in fig. 6, the barrier in sequence I of MoO is similar to that appearing in sequence II of fig. 4, when a more distant Cl atom is on the surface. Hence, the effect of MoO is more local in nature, compared to that of Cl.

In both sequences, our calculations favor the adsorption of parallel Di-σ CO in comparison with Top CO. This result can be explained on the basis of the electronic structure of Mo, an early transition metal. In previous works of Mehandru et al.,

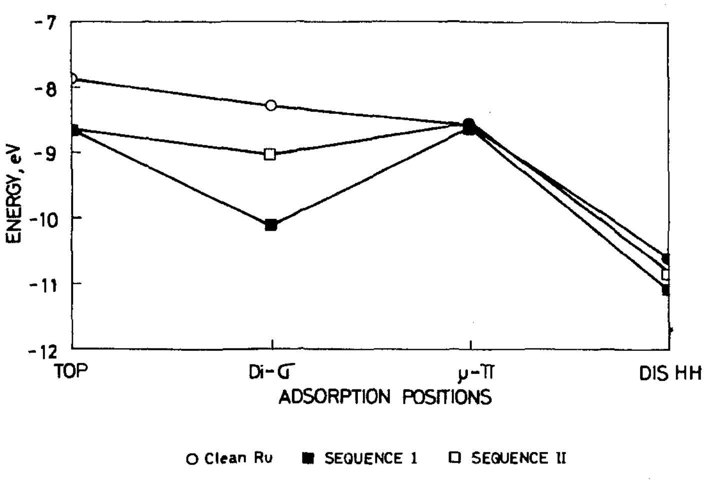

Fig.5. Binding energies for CO + MoO Ru(001) (eV).

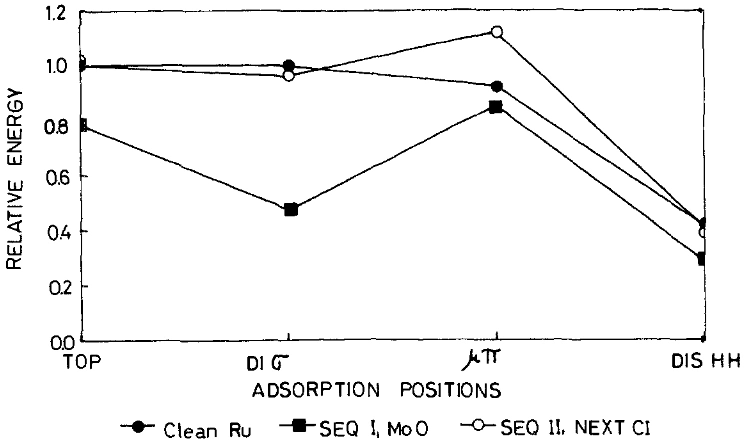

Fig.6. Comparison between the effect of Cl and MoO on CO adsoption.

the ability of CO to adsorb lying down on Cr(110) and on Pt_3Ti has been described theoretically in terms of a strong electron accepting ability of the d-electron deficient early transition metals [28]. Similar arguments have been discussed above.

If the foregoing mentioned activation energy for CO dissociation were lower than the energy for CO insertion into a metal–methyl bond, the promotion of the Di-σ configuration of the adsorbed CO molecule would allow the insertion of CO on a methyl group, and consequently the formation of higher alcohols like ethanol. Considering the possible interaction between a CO molecule and a methyl group during the alcohol synthesis, the repulsion could be lower when CO is in a Di-σ position (parallel to the surface) than when CO is Top (perpendicular to the surface). The reduction of the repulsive interactions results in a lowering of activation energies since the antibonding orbital formed upon interaction between the fragments usually is antisymmetric with respect to the center of the bond. Interactions with unoccupied metal orbital of the same symmetry lower the activation for the recombination or insertion (in our case this happens when Mo is present, a d-deficient electron metal, or when Cl is far away from the adsorption center and withdraws electron density from a contiguous Ru). In a study of CO insertion into a metal–methyl bond in organometallic complexes, Berke and Hoffmann found the interaction between the doubly occupied methyl σ-orbital and the doubly occupied 5σ-orbital of CO reduced because the antibonding orbital resulting from the two σ-orbitals is stabilized by the interactions with an empty d-orbital of the metal [11]. Hence, such parallel CO could be inserted to a CH_3–metal bond and yield an ethanol precursor, like it has been suggested for Ru/Al_2O_3 catalysts [29].

These theoretical results are consistent with previous experimental findings that under synthesis conditions chlorine-free $RuMo/SiO_2$ catalysts produce methanol and ethanol, metallic Mo catalysts also produce methanol and that ethanol is only obtained if Ru is present [23].

3. Conclusions

Semiempirical molecular orbital calculations were carried out on model clusters. The calculation predicts the presence of an activation energy for CO dissociation, which is greater for a Cl-doped Ru surface than for a MoO_x doped one, when equal distances CO–Cl and CO–MoO are considered.

The relative variations of the binding energy of CO to the surface of Ru confirm the strong poisoning effect of Cl and a somewhat promoting one of MoO_x.

For CO + MoO/Ru a reaction mechanism for alcohol formation can be pictured where a non-dissociated CO is subjected to a hydrogen addition. The relative stabilization of down-lying CO in relation to Top CO could account for the formation of higher alcohols by means of a CO insertion into a metal–CH_3 bond.

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