



## Enhanced reactivity of carbonyl compounds on MgO surface: A computational study

Galina P. Petrova, Georgi N. Vayssilov, Boris Galabov\*

Faculty of Chemistry, University of Sofia, Blvd. J. Bourchier 1, 1164 Sofia, Bulgaria

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### ABSTRACT

The paper analyzes the activation of carbonyl derivatives on regular MgO(001) surface based on appropriate reactivity descriptors derived from density functional theory computations. The carbonyl molecules adsorbed on the surface were found activated for nucleophilic addition reaction due to polarization of the C=O bond and increased electrophilicity, in particular of the carbon atom. The influence of the support was discussed in terms of electrostatic field and polarization of the electron density in the adsorbate. The substituent effect on reactivity for isolated and adsorbed molecules was also characterized.

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### 1. Introduction

Theoretical data on the properties of molecules adsorbed on the surface of a catalyst can provide valuable information on the specific modes of catalytic action and the activation of reactants. In the present work we examine how the reactivity of carbonyl compounds changes upon sorption on MgO catalyst. We evaluated by quantum mechanical computations several types of reactivity descriptors for isolated molecules and for the species sorbed on magnesium oxide. The characterization of molecules with the aid of reactivity descriptors is a major tool in studies on chemical reactions [1–17]. This approach towards quantifying reactivity demonstrates the power of chemical theory in evaluating the factors that influence reaction rates and mechanisms of reactions, mechanisms of catalytic activity, and other important inter- and intramolecular interactions. While theoretical computational methods have been employed extensively in modeling and analyzing the mechanisms of catalytic processes [18–20], the application of reactivity descriptors in characterizing catalytic phenomena, especially in heterogeneous catalysis, is limited [3,5,6] though appropriate reactivity indices have the potential to describe in quantitative terms what happens to molecules on the surface of a catalyst.

The aim of the present research is to apply appropriate reactivity indices in describing the activation of organic compounds on the surface of a heterogeneous catalyst. For this model study we selected the commonly used surface of a metal oxide: the MgO(001) surface [21–25]. Theoretical computations have been applied in describing the structure of the magnesia surface and different defects or various supported metal species on it [21–23].

Here, the adsorption of a series of carbonyl compounds on regular MgO(001) surface was theoretically modeled in order to define the influence of the support on the reactivity of these compounds. The effect of the catalyst was assessed by evaluating several reactivity descriptors for the adsorbed species. For many organic reactions the variation in reactivity is usually linked to structural changes influencing the reaction centers of the reactants (intramolecular factors) as well as the effects of media and possible homogeneous catalysts. On the other hand, in heterogeneous processes the catalyst's surface acts as an external factor that modifies the reactivity of the whole adsorbed molecule and its individual reaction centers mainly by the electrostatic field of the surface ions/atoms (and in some cases by coordination or hydrogen bonds). In this study we examine the simultaneous influence of both structural variations and oxide surface on reactivity descriptors for a series of carbonyl derivatives. We evaluated theoretically the electrophilicity index ( $\omega$ ), introduced by Parr et al. [4].  $\omega$  is a global reactivity index, defined in the framework of density functional theory. It characterizes the ability of molecule as a whole to acquire additional electronic charge. To characterize specific changes at the carbonyl group reaction center we used two alternative local reactivity

\* Corresponding author at: Faculty of Chemistry, University of Sofia, Blvd. J. Bourchier 1, 1164 Sofia, Bulgaria.

E-mail address: [galabov@chem.uni-sofia.bg](mailto:galabov@chem.uni-sofia.bg) (B. Galabov).

descriptors: the natural atomic charges [26,27] and the electrostatic potential at nuclei (EPN) [28,29] at the C and O nuclei. The latter parameter was found to be very accurate reactivity descriptor for the process of hydrogen bonding [12,13] and recently its application was successfully extended towards quantifying reactivity for number of basic organic reactions [14–16].

## 2. Theoretical model and method

All calculations were performed with Gaussian 09 program [30] using density functional method with the new hybrid functional M06-2X of Zhao and Truhlar [31]. This functional belongs to the M06 family of functionals that was designed to account for the van der Waals interactions and was applied successfully for modeling various systems, including adsorption on MgO surface [32]. For all atoms in the organic component a basis set 6-311++G(d,p) [33] was used. For the oxygen and magnesium centers of magnesia 6-311+G(d,p) and 6-31+G\* basis sets were employed, respectively. Our previous attempts to model adsorption of carbonyl compounds on MgO with other exchange-correlation functionals, B3LYP [34,35] and modified Perdew–Wang functional MPW1K [36], failed to find binding states since the calculated adsorption energies completely vanished for most of the compounds when one accounts for the BSSE corrections. Since precise experimental determination of the adsorption energies or vibrational spectra of the modeled carbonyl compounds on defect-free MgO(001) surface is not available, we cannot estimate directly the reliability of the hybrid functional M06-2X in describing the modeled systems. Such assessment has been, however, reported for CO adsorbed on defect-free MgO(001) surface [32]. The vibrational frequency shift of the stretching CO mode calculated with the same exchange-correlation functional is predicted accurately: calculated shift is  $+15\text{ cm}^{-1}$  versus experimental shift of  $+14\text{ cm}^{-1}$ . The binding energy of CO is found, however, overestimated by about 10 kJ/mol compared to the corresponding experimental value.

There are different approaches for modeling the metal-oxide surface as the most widely used methods are based on periodic computations and quantum-chemically treated cluster model embedded in point charges. We modeled the structure of the regular MgO(001) surface in the latter way as a two layered quantum (QM) cluster with stoichiometric composition  $\text{Mg}_{17}\text{O}_{17}$  surrounded by 24  $\text{Mg}^{\text{ECP}}$  ions and embedded into arrays of point charges. In order to avoid artificial polarization of the oxygen centers at the periphery of the embedded cluster 24  $\text{Mg}^{\text{ECP}}$  ions are situated next to the oxygen anions of the quantum-chemical cluster [37]. These ions are represented only by Stuttgart type effective core potential for magnesium [38] without basis functions and carry the standard charge of +2e. The upper layer of the QM cluster is with dimension  $5 \times 5$  ions while the lower one is smaller –  $3 \times 3$  ions units. The arrays of point charges representing the Madelung potential of the crystal structure is with dimensions  $13 \times 13 \times 6$  as the ions carry  $\pm 2e$  charge corresponding to the formal charges in an ideal ionic crystal. Only the positions of Mg and O ions in the central part of the quantum cluster, i.e.  $3 \times 3$  from the surface layer and the central Mg ion from the lower layer, were optimized. The other ions as well as the additional  $\text{Mg}^{\text{ECP}}$  species and the point charges were kept fixed. The obtained structure was applied for modeling the adsorption of the carbonyl compounds.

The adsorption energy,  $E_{\text{ads}}$ , of the carbonyl compounds  $\text{R}_2\text{CO}$  is calculated with respect to the optimized structure of the adsorbate free support and the corresponding isolated molecule according to Eq. (1).

$$E_{\text{ads}}(\text{R}_2\text{CO}) = E(\text{R}_2\text{CO}/\text{MgO}) - E(\text{MgO}) - E(\text{R}_2\text{CO}) \quad (1)$$

Thus, a negative value of the adsorption energy reveals stability of the adsorption complex and exothermicity of the studied process. The  $E_{\text{ads}}$  values, reported in Table 1, are corrected for BSSE with the value calculated for the quantum part of the MgO.

The discussion on the reactivity of the organic species is based on different characteristics of the molecules defined from the electron density distribution and the orbital energy of the valence electron levels. The atomic charges in the organic molecules in the gas phase and in the adsorption complexes were estimated by means of natural bond orbital analysis [27,39,40]. The electrophilicity index of the adsorbates,  $\omega$ , is calculated as proposed by Parr et al. [4] by the relation

$$\omega = \frac{\mu^2}{2\eta} \quad (2)$$

where  $\mu$  is the electronic chemical potential and  $\eta$  is the total hardness.  $\mu$  and  $\eta$  are estimated from the relationships

$$\mu = \frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2} \quad (3)$$

$$\eta \approx I - A \approx \varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}} \quad (4)$$

where  $I$  and  $A$  are ionization potential and electron affinity of the molecule, and  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{\text{LUMO}}$  denote the orbital energies of HOMO and LUMO. The electrostatic potential at nuclei was obtained as a component of the calculation of CHelpG charges [41].

## 3. Results and discussion

### 3.1. Adsorption energy and structures

The adsorption energies of all modeled adsorption complexes are provided in Table 1 together with some geometrical characteristics of the model systems. The optimized structures are shown in Fig. 1. The adsorption of the carbonyl derivatives on the magnesia surface results in formation of complexes with adsorption energy varying between  $-34.9$  and  $-60.0$  kJ/mol.

The formaldehyde and acetaldehyde molecules (Fig. 1) are oriented with the plane of the  $\text{sp}^2$  hybridized C atom perpendicular to the surface with carbonyl O atom coordinated to a surface Mg ion with O–Mg distance of 223–227 pm, while C–O<sub>s</sub> distance (O<sub>s</sub> denotes a surface oxygen ion) is above 300 pm. In presence of nucleophilic substituent, F, Cl, or OH, this substituent is coordinated to a Mg ion from the surface that keeps the whole molecule close to parallel to the surface with O–Mg and C–O<sub>s</sub> distances between 240 and 270 pm. The adsorption of the molecules results in a slight weakening of the carbonyl bond, as can be concluded from its elongation in the adsorption complex by 0.2–0.5 pm compared to the isolated molecules. The weakening of the carbonyl bond is also reflected in decrease of the C=O stretching frequency in the adsorbed species by 22–53  $\text{cm}^{-1}$  with respect to the computed values in the gas phase.

Direct comparison of the computationally obtained structural and IR data with the experiment is rather complicated since usually the applied experimentally MgO is not defect free but contains different oxygen vacancies or structural defects and on the other hand, experimental information about infrared spectra of carbonyl compounds adsorbed on MgO is scarcely found in the literature. The experimental analysis of acetone adsorbed on magnesia [42,43] shows that the C=O stretching mode is shifted by up to  $-40\text{ cm}^{-1}$  (with respect to acetone in gas phase) forming a Fermi doublet with an overtone. Our calculations reproduce correctly the direction and roughly the magnitude of the shift ( $-46\text{ cm}^{-1}$ ).

In order to evaluate reactivity of defect sites on MgO surface we modeled adsorption of formaldehyde and acetaldehyde on a neutral O vacancy. Since the energy for formation of such a vacancy calculated with respect to  $1/2\text{ O}_2$  molecule is rather high, 688 kJ/mol, the adsorption of  $\text{H}_2\text{CO}$  or  $\text{CH}_3\text{CHO}$  on the defect results

**Table 1**

Selected energetic, structural and spectral characteristics of the adsorption complexes of carbonyl derivatives on magnesia surface: adsorption energy  $E_{\text{ads}}$  (in kJ/mol); length of the C=O bond and deviation from the isolated species,  $\Delta R$ , and distance between C, O or X (X = F, Cl, O) atom from the organic molecule and  $O_s$  or Mg centers from the support (all distances in pm); uncorrected vibrational frequency of C=O stretching,  $\nu(\text{C=O})$ , and shift with respect to the corresponding isolated molecule,  $\Delta\nu(\text{C=O})$  (in  $\text{cm}^{-1}$ ); the intensity of the C=O vibrational mode (in  $\text{km/mol}$ ) is provided in *italics* in parentheses.

Compound	$E_{\text{ads}}$	C=O	$\Delta R$	C- $O_s$	O-Mg	X-Mg	$\nu(\text{C=O})$	$\Delta\nu(\text{C=O})$
H <sub>2</sub> CO	-36.1	120.1	0.4	314.2	223.6		1854 ( <i>103</i> )	-26
FHCO	-36.9	117.8	0.5	250.2	252.0	237.7	1904 ( <i>295</i> )	-53
ClHCO	-34.9	117.7	0.2	266.3	253.0	289.0	1882 ( <i>369</i> )	-31
CH <sub>3</sub> CHO	-38.9	120.5	0.5	331.0	227.1		1853 ( <i>187</i> )	-22
FCH <sub>2</sub> CHO	-41.2	120.1	0.4	260.9	240.6	227.4	1860 ( <i>168</i> )	-28
F <sub>2</sub> CHCHO	-45.6	119.8	0.6	256.5	246.6	231.2	1873 ( <i>140</i> )	-40
ClCH <sub>2</sub> CO	-44.2	119.9	0.3	267.7	239.1	285.4	1860 ( <i>155</i> )	-23
HOCH <sub>2</sub> CO	-60.0	120.1	0.3	264.3	242.0	217.8	1861 ( <i>173</i> )	-22
(CH <sub>3</sub> ) <sub>2</sub> CO	-47.6	121.3	0.8	274.8	229.4		1813 ( <i>212</i> )	-46

in restoration of the regular MgO surface with the carbonyl oxygen and the remaining H<sub>2</sub>C or CH<sub>3</sub>CH moieties remain adsorbed on the surface. The adsorption energies of H<sub>2</sub>CO and CH<sub>3</sub>CHO on the defect surface, -353 and -309 kJ/mol, respectively, are one order of magnitude higher than that on the regular surface. Thus, even in presence of oxygen vacancy defects on MgO surface, after adsorption of the carbonyl compounds these defects will be immediately filled by the carbonyl oxygen, the regular MgO surface will be recovered and the defect will not have further influence on the process. The only influence that such defect could have on the adsorption of the carbonyl compounds is connected with eventual increase of the experimentally measured initial adsorption energy.

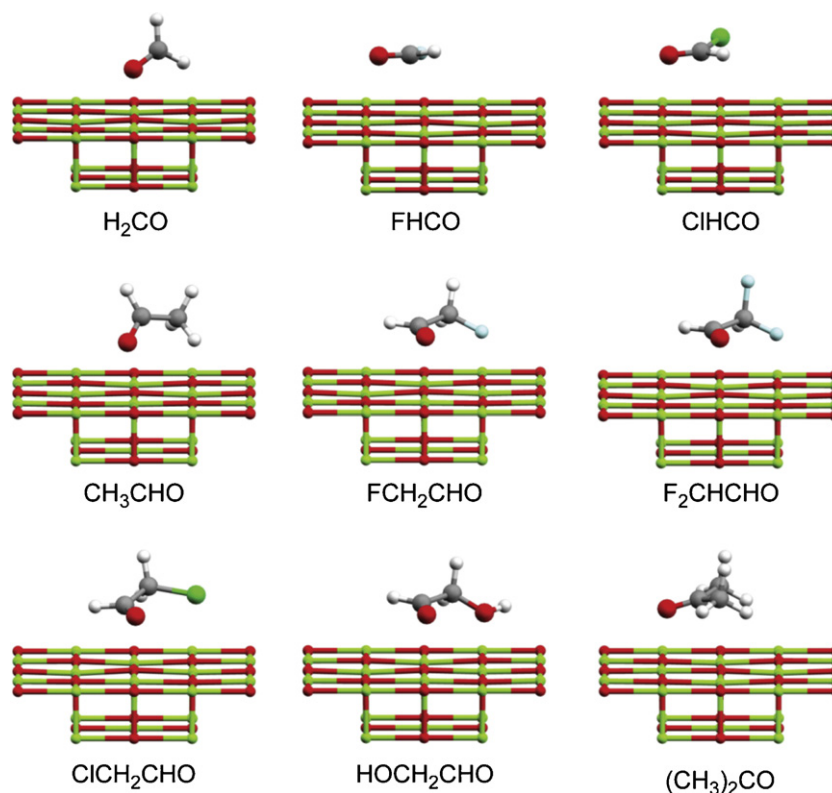
### 3.2. Influence of the adsorption on electron density distribution and reactivity

The changes in properties of the carbonyl compounds accompanying the transition from isolated molecules to adsorbed on the MgO surface species were followed by examining the electron pop-

ulation via NBO computations as well as by analyzing the variations of the electrostatic potential at the carbon ( $V_C$ ) and oxygen ( $V_O$ ) atoms of the carbonyl functionality. The theoretically evaluated NBO atomic charges ( $q_C$ ,  $q_O$ ) and EPN values for the C=O group in the studied derivatives are presented in Tables 2 and 3. Other theoretical data on the variations of the charge density and electronic parameters for the studied molecules adsorbed on the surface of the catalyst as well as shifts of key parameters for the carbonyl group associated with the adsorption process are reported in Tables 4–6.

The changes of the C and O atomic charges in the studied compounds due to adsorption on the metal-oxide surface are smaller than 0.1 e. The charges of the carbonyl C atoms increase by 0.04–0.09 e, while the carbonyl O atoms become slightly more negatively charged by -0.01 to -0.06 e. Thus, the adsorption on the magnesia surface induces additional polarization of the carbonyl group.

More reliable data for the electron density rearrangements accompanying the sorption process could be obtained from the electrostatic potential at nuclei values (Table 3). As already empha-



**Fig. 1.** Optimized structures of various adsorption complexes of the carbonyl compounds on the model MgO surface. Only the quantum fragment of the surface is shown. Color coding: O – red, Mg – light green, C – grey, H – white, Cl – green, F – light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2**  
NBO atomic charges (in electrons) for the C=O group in isolated and adsorbed carbonyl derivatives.

Compound	<i>q</i> isol.		<i>q</i> ads.		$\Delta q^a$		$\sum q^b$
	<i>q</i> <sub>C</sub>	<i>q</i> <sub>O</sub>	<i>q</i> <sub>C</sub>	<i>q</i> <sub>O</sub>	<i>q</i> <sub>C</sub>	<i>q</i> <sub>O</sub>	
H <sub>2</sub> CO	0.293	-0.497	0.351	-0.511	0.058	-0.014	0.096
FHCO	0.760	-0.507	0.799	-0.533	0.039	-0.025	0.015
ClHCO	0.399	-0.472	0.468	-0.485	0.070	-0.013	0.151
CH <sub>3</sub> CHO	0.445	-0.528	0.499	-0.538	0.054	-0.010	0.117
FCH <sub>2</sub> CHO	0.412	-0.514	0.477	-0.534	0.065	-0.019	0.139
F <sub>2</sub> CHCHO	0.378	-0.470	0.435	-0.532	0.057	-0.063	-0.129
ClCH <sub>2</sub> CO	0.431	-0.505	0.502	-0.529	0.070	-0.024	0.196
HOCH <sub>2</sub> CO	0.438	-0.526	0.499	-0.537	0.061	-0.011	0.160
(CH <sub>3</sub> ) <sub>2</sub> CO	0.579	-0.555	0.665	-0.598	0.086	-0.042	0.147

<sup>a</sup>  $\Delta q = q(\text{adsorbed}) - q(\text{isolated})$ .

<sup>b</sup>  $\sum q$  – total charge of the organic moiety (positive value is equivalent to charge transfer to the surface).

**Table 3**  
Electrostatic potential at nuclei (in a.u.) for the carbonyl carbon and oxygen atoms in isolated and adsorbed molecules.

Compound	<i>V</i> isol.		<i>V</i> ads.		$\Delta V(\text{total})^a$		$\Delta V(\text{total})^b$	
	<i>V</i> <sub>C</sub>	<i>V</i> <sub>O</sub>	<i>V</i> <sub>C</sub>	<i>V</i> <sub>O</sub>	$\Delta V$ <sub>C</sub>	$\Delta V$ <sub>O</sub>	$\Delta V$ <sub>C</sub>	$\Delta V$ <sub>O</sub>
H <sub>2</sub> CO	-14.6732	-22.3440	-14.6398	-22.3024	0.0335	0.0415	0.0158	-0.0029
FHCO	-14.5827	-22.3197	-14.5519	-22.2976	0.0308	0.0221	0.0209	-0.0079
ClHCO	-14.6024	-22.3095	-14.5771	-22.2894	0.0253	0.0201	0.0137	-0.0079
CH <sub>3</sub> CHO	-14.6773	-22.3600	-14.6422	-22.3201	0.0352	0.0399	0.0185	-0.0026
FCH <sub>2</sub> CHO	-14.6615	-22.3386	-14.6266	-22.3180	0.0349	0.0207	0.0231	-0.0162
F <sub>2</sub> CHCHO	-14.6470	-22.3198	-14.6173	-22.3061	0.0297	0.0137	0.0187	-0.0192
ClCH <sub>2</sub> CO	-14.6565	-22.3362	-14.6248	-22.3166	0.0317	0.0196	0.0178	-0.0177
HOCH <sub>2</sub> CO	-14.6763	-22.3532	-14.6363	-22.3268	0.0399	0.0264	0.0249	-0.0124
(CH <sub>3</sub> ) <sub>2</sub> CO	-14.6791	-22.3731	-14.6413	-22.3424	0.0377	0.0307	0.0206	-0.0148

<sup>a</sup>  $\Delta V(\text{total}) = V(\text{adsorbed}) - V(\text{isolated})$ .

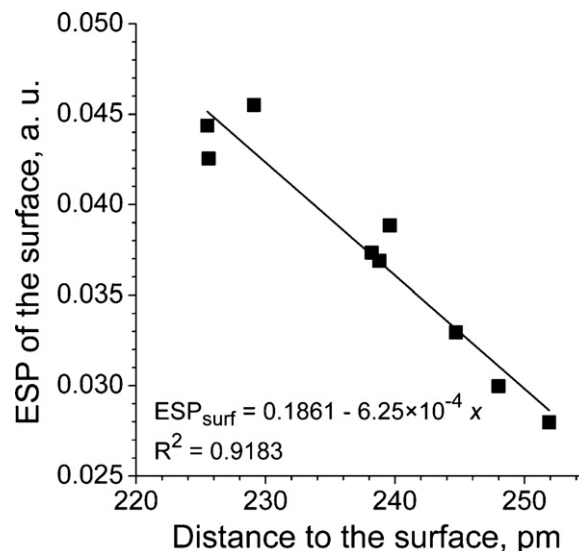
<sup>b</sup> Differences corrected for the electrostatic field of the adsorbent at the position of the nuclei, corresponding to the polarization contribution due to adsorption,  $\Delta V(\text{polarization})$  in Eq. (5).

sized, the EPN values are obtained without any further constraints or approximations in their evaluation and have the same accuracy as the wave function employed. The dominant contribution to the *V*<sub>C</sub> and *V*<sub>O</sub> values comes from the electron density close to the respective atomic positions. The model-independent EPN values reflect, therefore, the fluctuations of charge densities in close vicinity of the respective nuclei. In addition to the polarization effect of the adsorbent on the electron density distribution in the carbonyl group in the case of adsorbed species, the electrostatic field of the support has also a direct “static” contribution to the EPN value:

$$\Delta V(\text{total}) = \Delta V(\text{polarization}) + \Delta V(\text{static}) \quad (5)$$

The static contribution depends only on the position of the nuclei above the surface: in horizontal position the potential is different when the atom is above Mg<sup>2+</sup> or above O<sup>2-</sup> surface center, while in vertical direction the field of the surface simply decreases with the distance from the surface. However, the electrostatic field of the surface does not depend on the presence of the adsorbate when the structure of the surface is not modified. In order to estimate this contribution for the adsorbed structures, we calculated the electrostatic potential at the positions of all nuclei in the adsorbed molecule without the molecule itself. The obtained values are always positive and vary between 0.010 and 0.018 a.u. for the carbonyl C atom position and 0.028 and 0.046 a.u. for O. For the latter values we found a tentative correlation between the electrostatic field of the adsorbent at the position of the carbonyl oxygen and the distance between this oxygen and the MgO surface (Fig. 2). Using the calculated values of the static contributions, we determined the “polarization” contribution into the  $\Delta V(\text{total})$  (the corresponding values are reported as corrected difference in the last two columns of Table 3).

The results obtained are quite revealing. It is seen that the adsorption process results in reduced electron density at the carbonyl carbons for all studied derivatives. These changes suggest substantial increase in the partial positive charge at the carbonyl carbon, which leads to higher susceptibility of the C center to nucleophilic attack. Interestingly, the total shifts of *V*<sub>O</sub> values for the adsorbed species suggest reduced electron density at the carbonyl oxygen as well. However, when the static contribution of the surface is taken into account, then the shifts of *V*<sub>O</sub> values of the



**Fig. 2.** Correlation between the distance of the carbonyl oxygen atom from the oxide surface and the value of the electrostatic potential of the support at the position of that atom.

**Table 4**

Effect of substituent on the NBO atomic charges (in electrons) in isolated and adsorbed carbonyl derivatives calculated with respect to formaldehyde in corresponding state (isolated or adsorbed).

Compound	$\Delta q$ isol. <sup>a</sup>		$\Delta q$ ads. <sup>b</sup>		$\Delta \Delta q$ ads. <sup>c</sup>	
	$\Delta q_C$	$\Delta q_O$	$\Delta q_C$	$\Delta q_O$	$\Delta \Delta q_C$	$\Delta \Delta q_O$
H <sub>2</sub> CO	0.000	0.000	0.000	0.000	0.000	0.000
FHCO	0.466	-0.010	0.448	-0.022	-0.018	-0.012
ClHCO	0.105	0.025	0.117	0.026	0.012	0.001
CH <sub>3</sub> CHO	0.152	-0.031	0.148	-0.027	-0.003	0.004
FCH <sub>2</sub> CHO	0.119	-0.017	0.126	-0.023	0.008	-0.005
F <sub>2</sub> CHCHO	0.085	0.028	0.084	-0.021	0.000	-0.049
ClCH <sub>2</sub> CO	0.138	-0.008	0.151	-0.018	0.013	-0.010
HOCH <sub>2</sub> CO	0.145	-0.029	0.148	-0.026	0.003	0.003
(CH <sub>3</sub> ) <sub>2</sub> CO	0.286	-0.058	0.314	-0.087	0.029	-0.029

<sup>a</sup>  $\Delta q$  isol. =  $q$  (R<sub>2</sub>C=O) isol. -  $q$  (H<sub>2</sub>C=O) isol.

<sup>b</sup>  $\Delta q$  ads. =  $q$  (R<sub>2</sub>C=O) ads. -  $q$  (H<sub>2</sub>C=O) ads.

<sup>c</sup>  $\Delta \Delta q$  ads. =  $\Delta q$  ads. -  $\Delta q$  isol.

carbonyl oxygen atoms in all compounds due to the polarization of the electron density in the adsorbate are negative, which indicates increase of the negative charge, and respectively nucleophilicity of these centers. Thus, employing the corrected differences of the calculated EPN values for the adsorbed carbonyl compounds, we found qualitative correlation with the trends determined from the NBO charges. The eventual partial quantitative disaccord between the theoretical data for the NBO charges and the EPN values can be attributed to the approximate nature of atomic charges, the derivation of which always involves various assumptions and approximations. The net effect of the electronic rearrangements in the adsorbed molecules and, in particular, at the carbonyl group clearly indicates increased polarity of the C=O bond due to increase of both the positive charge at the carbon atom and the negative charge at the oxygen. Such a change may well explain the increased reactivity of the adsorbed molecules compared to the isolated species.

### 3.3. Influence of the substituent on the electron density distribution and reactivity

The theoretical results obtained allow also the examination of the effect of substituents on the properties of isolated and adsorbed compounds. The variations of electronic parameters induced by the various substituents at the carbonyl group are well illustrated in Tables 4 and 5. Table 4 shows the shifts of NBO atomic charges of the carbonyl carbon and oxygen along the nine studied derivatives, both isolated and adsorbed on MgO surface. As expected, the strongly electronegative fluorine substituent invokes considerable positive increase of the charge on the immediate neighboring carbon atom (+0.466 e). The variations of the charges for compounds with other substituents, however, are not well reflected by the

NBO charges. Thus, chlorine appears to have smaller effect than the methyl group, while the two methyl groups (in acetone) are predicted to induce considerable positive change at the carbon atom (+0.283).

Survey of the variations of the atomic charges for the adsorbed species with respect to the adsorbed unsubstituted parent molecule of formaldehyde reveals similar shifts as those of the isolated molecules. As shown in the last two columns of Table 4, the difference in the substituent effect on the NBO charges in the isolated and in the adsorbed molecules ( $\Delta \Delta q$ ) is minor, i.e. the adsorption does not modify considerably the substituent effect on the reaction center.

A consistent picture of the substituent influence on the reaction centers comes from the examination of the variations of EPN values. Table 5 shows the shifts of  $V_C$  and  $V_O$  in the isolated and adsorbed molecules compared to the respective values in HCHO. In the free molecules strong positive charge shifts at the carbonyl carbon are found for FCHO (+0.0905 a.u.) and ClCHO (+0.0708 a.u.). Contrary to the NBO predictions for FCHO, both F and Cl substituents induce smaller but distinctive reduction of electron density at the carbonyl oxygen as well. This result is quite logical in view of the strong electron withdrawing effect of these groups. Increased electron densities at both C and O atoms for substitutions with methyl groups are predicted by the variations of the corresponding  $V_C$  and  $V_O$  values. The effect of the second methyl group in acetone and the electron donating hydroxymethyl group in 2-hydroxyacetaldehyde is similar, i.e. decrease of EPN at both C and O atoms. The electron-withdrawing effect of F<sub>2</sub>CH, FCH<sub>2</sub>, and ClCH<sub>2</sub> groups, resulting in reduction of the electron density on carbonyl C and O atoms, increases the EPN at both centers.

As described above, the examination of the electrostatic potential at nuclei values for the adsorbed molecules reveals increased

**Table 5**

Effect of substituent on the EPN (in a.u.) for the carbonyl C and O atoms in isolated and adsorbed carbonyl derivatives calculated with respect to formaldehyde in corresponding state (isolated or adsorbed). The shift of the C=O vibrational frequency  $\Delta \nu_{C=O}$  (in cm<sup>-1</sup>) due to the substituent in the isolated molecules is also provided.

Compound	$\Delta V$ isol.		$\Delta V$ ads.		$\Delta \Delta V$ ads.		$\Delta \nu_{C=O}$
	$\Delta V_C$	$\Delta V_O$	$\Delta V_C$	$\Delta V_O$	$\Delta \Delta V_C$	$\Delta \Delta V_O$	
H <sub>2</sub> CO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0
FHCO	0.0905	0.0242	0.0879	0.0048	-0.0027	-0.0194	77
ClHCO	0.0708	0.0344	0.0627	0.0130	-0.0082	-0.0214	33
CH <sub>3</sub> CHO	-0.0041	-0.0160	-0.0024	-0.0177	0.0017	-0.0016	-5
FCH <sub>2</sub> CHO	0.0117	0.0053	0.0132	-0.0156	0.0015	-0.0209	7
F <sub>2</sub> CHCHO	0.0262	0.0241	0.0225	-0.0037	-0.0038	-0.0278	33
ClCH <sub>2</sub> CO	0.0167	0.0078	0.0150	-0.0142	-0.0017	-0.0219	3
HOCH <sub>2</sub> CO	-0.0030	-0.0092	0.0035	-0.0244	0.0065	-0.0152	4
(CH <sub>3</sub> ) <sub>2</sub> CO	-0.0058	-0.0291	-0.0015	-0.0400	0.0043	-0.0109	-22

<sup>a</sup>  $\Delta V$  isol. =  $V$  (R<sub>2</sub>C=O) isol. -  $V$  (H<sub>2</sub>C=O) isol.

<sup>b</sup>  $\Delta V$  ads. =  $V$  (R<sub>2</sub>C=O) ads. -  $V$  (H<sub>2</sub>C=O) ads.

<sup>c</sup>  $\Delta \Delta V$  ads. =  $\Delta V$  ads. -  $\Delta V$  isol.

**Table 6**  
Electrophilicity index  $\omega$  (in eV) for isolated and adsorbed carbonyl derivatives.

Compound	$\omega$ isol.	$\omega$ ads.	$\Delta\omega^a$	$\Delta\omega^b$	$\Delta\omega^c$
H <sub>2</sub> CO	1.3104	1.8923	0.5820	0.0000	0.0000
FHCO	1.4208	1.7489	0.3281	0.1104	-0.1435
ClHCO	1.5605	1.8685	0.3080	0.2502	-0.0238
CH <sub>3</sub> CHO	1.1690	1.5630	0.3940	-0.1414	-0.3293
FCH <sub>2</sub> CHO	1.3501	1.7152	0.3651	0.0398	-0.1772
F <sub>2</sub> CHCHO	1.6445	1.9244	0.2800	0.3341	0.0321
ClCH <sub>2</sub> CO	1.3856	1.7507	0.3651	0.0753	-0.1416
HOCH <sub>2</sub> CO	1.2778	1.7023	0.4245	-0.0326	-0.1900
(CH <sub>3</sub> ) <sub>2</sub> CO	1.1814	1.4384	0.2571	-0.1290	-0.4539

<sup>a</sup>  $\Delta\omega = \omega$  ads. –  $\omega$  isol.

<sup>b</sup>  $\Delta\omega = \omega$  (R<sub>2</sub>C=O) isol. –  $\omega$  (H<sub>2</sub>C=O) isol.

<sup>c</sup>  $\Delta\omega = \omega$  (R<sub>2</sub>C=O) ads. –  $\omega$  (H<sub>2</sub>C=O) ads.

polarity of the carbonyl group upon adsorption on the MgO surface. The variations of the EPN values at the carbonyl carbon and oxygen atoms with respect to the adsorbed HCHO molecule are similar to those obtained for the isolated molecules. The variations of the electron density at the carbonyl oxygen, compared to the unsubstituted HCHO molecule, however, depend strongly on the interaction of the respective derivatives with the catalyst surface. In all substituted acetaldehydes the substituent causes negative shift of the EPN at the carbonyl O due to the polarization of the carbonyl group. These results are logical in connection with the interactions of the modeled molecule with the surface of the adsorbent, i.e., the adsorption does not influence strongly the substituent effect on the carbonyl group.

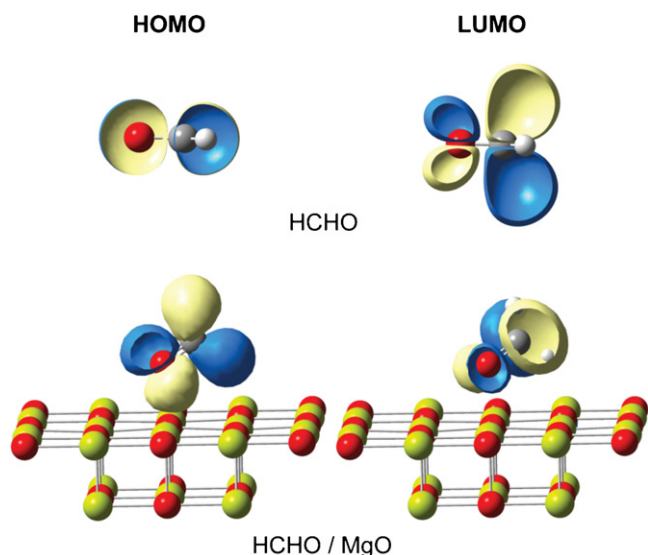
The influence of the different substituents on the electron density distribution in the molecules affects also the carbonyl stretching frequency in the studied compounds. The shifts for substituted formaldehyde are 77 and 33 cm<sup>-1</sup> for F and Cl, respectively, while the magnitude of the shift decreases notably when the halogen is bound at the methyl group of the acetaldehyde, 7, 3, and 4 cm<sup>-1</sup>, for monosubstituted F, OH, and Cl acetaldehyde, respectively. The second F substituent in acetaldehyde increases the frequency shift to 33 cm<sup>-1</sup>. On the other hand, one and two substituent methyl groups in acetaldehyde and acetone results in weak negative shift of the C=O frequency by -5 and -22 cm<sup>-1</sup>.

Finally, the reactivity of the adsorbed molecules can be analyzed with the aid of the Parr electrophilicity index,  $\omega$  [4], which characterizes the reactivity of the molecule as a whole. Since the electrophilic center in the series of compounds studied is the C=O group, the  $\omega$  index describes essentially its ability to react with nucleophiles. The obtained values (Table 6) clearly show an increase of the electrophilic power of the carbonyl group in the sorbed species compared to the isolated molecules by 0.25–0.58 eV. The adsorption of the organic molecules on the magnesia surface results in slight stabilization of the frontier orbitals by ca. 0.27–0.81 eV (the shape of the frontier orbitals in gas phase and on support are shown in Fig. 3 on the example of formaldehyde molecule). The influence of the substituent on the electrophilicity index both in isolated and adsorbed molecules follows the trends observed for the EPN values.

#### 4. Conclusions

The computational investigation of the adsorption of a series of carbonyl compounds on MgO surface showed that these organic molecules can form stable adsorbed complexes with adsorption energy higher than 30 kJ/mol in absolute value. As can be expected, the adsorption on the metal oxide surface results in activation of the carbonyl group, connected with different effects: direct electrostatic field of the support, polarization of the electron density in the carbonyl compound on the surface, charge transfer from/to the surface, specific effects of the substituents at the carbonyl group.

The adsorption on magnesia surface increases the electrophilicity of the carbonyl compounds as can be concluded from the increase of the corresponding index  $\omega$  by 0.25–0.58 eV with respect to the isolated molecules. The analysis of the variations of the electrostatic potential at C and O nuclei of the carbonyl group also suggested activation of this group due to polarization by the surface ions. The  $V_C$  values show substantial increase of the partial positive charge at the carbonyl carbon leading to higher susceptibility to nucleophilic attack. The polarization contribution in the  $V_O$  shifts (determined by subtraction of the static contribution) of the carbonyl O atoms in all compounds is negative, which indicates increase of the negative charge, and respectively of the nucleophilicity of these centers. If the reactant attacking the adsorbed carbonyl compound is at similar vertical position with respect to the surface, this reactant will be exposed to the same electrostatic field of the surface as the carbonyl derivative. In this case, important for the reactivity will not be the absolute values of the EPN at the reaction centers in the two molecules but the corrected values, in which the contribution of the static field of the surface is subtracted. The calculated polarization contributions to EPN are more appropriate reactivity descriptors for such adsorbed species than the total EPN values. The calculated NBO charges follow the qualitative conclusions based on the polarization contribution in



**Fig. 3.** Frontier molecular orbitals of formaldehyde in the gas phase and adsorbed on MgO surface. Color coding: O – red, Mg – light green, C – grey, H – white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the calculated EPN values for the carbon and oxygen centers in the adsorbed carbonyl compounds.

The calculated shifts of EPN values induced by substituents at the carbonyl group are in agreement with the expected trends for both isolated and adsorbed molecules. It was also shown that the adsorption does not influence considerably the substituent effects on the reaction center. The magnitude of the change in the EPN or NBO charge of the atoms in the carbonyl group due to presence of a substituent, attached to the carbonyl C atom, is usually higher than the magnitude of the change achieved due to the adsorption.

In summary, the adsorbed carbonyl molecules on the MgO surface are activated (with polarized C=O bond and increased electrophilicity of the C atom) for nucleophilic addition reactions.

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