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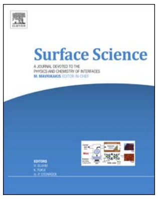

The role of Zn^{2+} dopants in the acid-basic catalysis on MgO(001) surface: *Ab initio* simulations of the dissociative chemisorption of R-O-R′ and R-S-R′ (R, R′ = H, CH_3, C_2H_5)

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ABSTRACT

Ab initio calculations were performed to study the effect of the Zn^{2+} dopant on the reactivity and the catalytic activity of the MgO(001) surface toward molecular adsorption and dissociation reactions of the H_2O, H_2S, CH_3CH_2OH, CH_3CH_2SH and CH_3SCH_3 molecules. The electronic analysis showed that Zn^{2+} cation increased the reactivity of the surface locally. All molecules dissociate on both surfaces except for water and ethanol which only dissociate on the MgO:Zn(001) surface, confirming the increased reactivity in this surface. The $\Delta G°$ for the dissociation reactions of the CH_3CH_2SH and CH_3SCH_3 molecules on pure MgO(001) surface is positive in the entire temperature range. On the other hand, the $\Delta G°$ for H_2S molecule is negative until 148.7 °C. In the case of the MgO:Zn(001) surface, the CH_3CH_2SH molecule dissociates in the entire temperature range and, for H_2S molecule, the dissociation is spontaneous until 349.7 °C. The rate constants obtained for the dissociation reactions were very large because the reaction barriers are very low in both surfaces for all the studied molecules, except for CH_3SCH_3 molecule. The Zn-doped MgO(001) surface, besides being more reactive, presented a better catalytic activity than the MgO(001) surface for the dissociation of this molecule.

1. Introduction

During the last decades, strong incentives have been done for the development of more efficient acid-basic catalysts. Systems which drew much attention are the metal oxides, zeolites, mixed oxides obtained by thermal decomposition of layer double hydroxides or hydroxy double salts [1,2]. Metal oxides such as the magnesium oxide (MgO) played an important role serving as components as well as supports and active catalytic agents for many processes, such as methanol and ethanol decomposition, oxidative coupling of methane, water-gas shift reactions and hydrodessulfurization of petroleum [3,4].

MgO easily cleaves along the direction [001], which is the most stable surface [5]. This surface presents the same number of cations and anions, both pentacoordinated, and these surface sites, even with extremely low reactivity, are very important for various reactions in the catalysis field [6,7]. The presence of impurities or defects is common on these surfaces and substantially increases the reactivity of the oxides. Surface defects like, corners, or even vacancies or dopant atoms, are the ones where the most reactions occur [8,9]. These sites are able to present acid/basic behavior different from the regular surface sites and they are directly related to the activity and the selectivity of the surface towards the specific reaction pathway [10].

MgO was already used as the base for the reactional design of new catalysts or supports by inserting metal dopants in order to improve the acid-basic characteristics. These catalytic species modify the cation shift in the $Mg^{2+}O^{2-}$ system, thus generating a charge redistribution on the surface [3,11,12]. The strong electrostatic interaction between the point defects on the oxide surface and the adsorbed molecules is essential to the heterolytic dissociation of covalent bonds.

MgO is an insulator whereas ZnO is a semiconductor. When both phases coexist, the mixed phase collectively exhibits useful properties of both oxides [13]. The increase of the reactivity of various oxides was observed upon doping and it also attracted interest in different respects. It was found that the antibacterial activity increased with

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the increase of the Zn content in MgO [14]. Metal-doped MgO as $Zn_xMg_{1-x}O(100)$ and $Cr_xMg_{1-x}O(100)$ was used as catalysts with a high efficiency for the destruction of NOx compounds [3]. Doped metal oxides (Zn-doped MgO, Cs-promoted MgO) were also used as catalysts for the transesterification of vegetables oil for biodiesel production [12,15] and for the activation of methane [10]. The C and N-doped MgO(001) surfaces were investigated towards the molecular and the atomic adsorption using the CO molecule and atomic O [16]. Many industrial operations in which oxides are used as sorbents for the removal or destruction of sulfur-containing molecules. In this context, the adsorption and the dissociation processes of H_2S on Ni-doped MgO(100) have been studied [17].

The mixed oxides are considered promising catalysts due to the preparation facility, the high specific area and the pore volume [18,2,19]. Moreover the variety of compositions that can be achieved modifies the distribution and the strength of the sites in the material, and this can significantly alter the catalytic properties of the derived mixed oxides [20]. These properties make it useful as a support for the hydrotreating process [4]. Since the mixed oxides present low crystallinity and, consequently, their structure was not yet refined and reported in the literature, an alternative for the model design of mixed oxides using computational simulations can be done by the insertion of metallic dopants on MgO(001) surface as reported by Alvim et al. [7].

To understand the effect of the insertion of the Zn dopant metal in the reactivity and catalytic activity of the MgO(001) surface in some important processes cited above such as hydrodessulfurization and transesterification, we chose the following molecules H_2O, H_2S, CH_3CH_2OH, CH_3CH_2SH and CH_3SCH_3 to investigate the adsorption and possible intermediates formed by dissociation of these molecules in reactions in which they are involved. Adsorbed or dissociated water molecules in the metal oxide surfaces affect the surface chemistry of these metal oxides and are also very important in the kinetics of hydrolysis reactions. For example, the water molecule can poison some catalysts especially in transesterification reactions and the fatty acid methyl esters (FAME) obtained by these processes cannot present a significant amount of impurities including water. Some authors suggest that the research of intelligent catalysts, which catalyze the reaction and remove the water formed as byproduct, may circumvent this problem [21,22]. Furthermore, the circumvention of the water removal would also cheapen the biodiesel production, since it requires a somewhat pure feedstock. The ethanol is also an important molecule for the transesterification (ethanolysis) of triglycerides. Yan et al. [23] reports that, differently from the esterification reactions, the ethanol molecules are adsorbed on the surface and their protons interact with the basic sites thus facilitating the formation of an alkoxide. In oil feedstocks, the sulfur is present as thiols, sulfides, disulfides and thiophenes and the hydrodessulfurization process consists of the removal of sulfur atoms from these compounds by a reduction treatment. Therefore, in this work, we performed *ab initio* calculations to study the MgO(001) and Zn-doped MgO(001) surfaces. The changes in the electronic and acid-basic properties were investigated by Bader charge analysis, density of states calculations (DOS) and projected density of states (PDOS), and the reactivity and catalytic activity of the surfaces were verified through the adsorption and dissociation reactions of the H_2O, H_2S, CH_3CH_2OH, CH_3CH_2SH and CH_3SCH_3 molecules on the MgO(001) and MgO:Zn(001) surfaces. We computed the Gibbs free energy variation, activation energies and rate constants of the reactions. For the sake of simplicity, MgO:Zn(001) surface was also named as Zn-doped MgO(001) surface.

2. Proposed mechanisms

To investigate the adsorption and the dissociation reactions of the H_2O, H_2S, CH_3CH_2OH, CH_3CH_2SH and CH_3SCH_3 molecules on the MgO(001) and Zn-doped MgO(001) surfaces and to verify the effect of the Zn dopant metal on the electronic properties, reactivity and catalytic activity of the MgO(001) surface, we proposed a mechanism consisting of two steps. In the first step, we examined the adsorption reaction of these molecules on both surfaces, and in the second one, the dissociation reaction. The reactions R1 and R2 correspond to the adsorption and the dissociation reactions, respectively. In order to complement this nomenclature, we used the letter P for the reactions on the pure MgO(001) surface and D for the reactions on the Zn-doped MgO(001) surface. For instance, the reactions for H_2S are represented below.

Step 1

$$(R1_P)\,MgO(001)_{(s)} + H_2S_{(g)} \rightarrow MgO(001) - H_2S_{(s)}\,(R1_D)\,MgO$$
$$: Zn(001)_{(s)} + H_2S_{(g)} \rightarrow MgO$$
$$: Zn(001) - H_2S_{(s)}$$

Step 2

$$(R2_P)\,MgO(001) - H_2S_{(s)} \rightarrow MgO(001) - [H^+][HS^-]_{(s)}\,(R2_D)\,MgO$$
$$: Zn(001) - H_2S_{(s)} \rightarrow MgO$$
$$: Zn(001) - [H^+][HS^-]_{(s)}$$

The products of the ($R1_P$) and ($R1_D$) reactions are the systems formed by the adsorbed molecules on the surfaces, represented above by MgO(001)-$H_2S_{(s)}$ and MgO:Zn(001)-$H_2S_{(s)}$, respectively. The adsorbed molecules react with the surfaces and dissociate, then the products are formed in ($R2_P$) and ($R2_D$), represented above by the systems MgO(001)-$[H^+][HS^-]_{(s)}$ and MgO:Zn(001)-$[H^+][HS^-]_{(s)}$, respectively.

3. Theoretical methodology

All *ab initio* calculations were performed using the Quantum ESPRESSO package [24] which is based on the density-functional theory (DFT) [25,26] with periodic boundary conditions [27]. The exchange-correlation potential was described by the PW91 Generalized Gradient Approximation (GGA) [28], and the core electrons were treated with Vanderbilt ultrasoft pseudopotentials [29]. Kohn-Sham orbitals were expanded in a plane wave basis set up to a kinetic energy cutoff of 60 Ry and with a cutoff of 480 Ry for the charge density. The electron density was obtained at the Γ point in the first Brillouin-Zone of the supercells.

The MgO structure has cubic symmetry, $a=b=c=4.21$ Å and $\alpha=\beta=\gamma=90°$, belongs to $Fm3m$ spatial group. In order to construct the slab model of MgO, the bulk was first optimized. The calculated lattice constant was 4.26 Å, which is in good agreement with the experimental data, with a relative error around 1.2% [30]. The slab model of the Mg(001) surface was also constructed using periodic boundary conditions. In this approximation, the original cell was replicated in the directions *ab* and a vacuum layer of 15 Å was added along the axis *c*. This vacuum was placed on the top of the surface to ensure that there are no interactions between the periodic images perpendicular to the surface. Our slab model presents a three-layer-thick slab with 18 atoms on the surface, consisting of 9 cations and 9 anions. In the case of the MgO:Zn (001) surface, one Mg atom was exchanged by one Zn atom in the first layer, called Zn-doped center, then giving the total dopant concentration of 11% with respect to the total Mg atoms on this same monolayer. We verified that the second monolayer was not affected by the dopant in the case of the doped surface model. Therefore, in our model surfaces, only the first layer and the molecules were allowed to relax during the geometric optimization. The other atoms of MgO(001) and MgO:Zn(001) models were held at their theoretical bulk positions. The structures were allowed to relax until all residual force components were less than 10^{-3} Ry Bohr^{-1} and the total energy difference was less than 10^{-4} Ry. The free molecules were optimized using a cubic supercell of 15 Å.

A Bader charge analysis was conducted using a grid-based algo-