Ethylene glycol interaction on alkaline earth oxides: A periodic DFT study

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ABSTRACT

The present paper describes the interaction of ethylene glycol CH_2OH–CH_2OH with alkaline earth oxide basic catalysts MO (M = Mg, Ca, Sr, Ba) from periodic DFT calculations. The geometry of adsorption depends on the nature of the metallic site: on MgO the alcohol groups bind to the metal sites on quasi-top positions, while on CaO, SrO and BaO the molecule is located on bridging positions. The adsorption is exothermic and the strength correlates with the basicity of the alkaline earth oxide, the more basic the substrate, the more exothermic the adsorption energy: MgO < CaO < SrO < BaO. The glycol molecule deprotonates to form surface alkoxy groups bound to the metal sites. The extent of such deprotonation is also correlated to the basicity of MO:MgO (completely protonated) < CaO (partially protonated) < SrO (completely deprotonated) = BaO (completely deprotonated). Defects, modeled for a stepped CaO slab, are found to enhance the strength of the interaction and the deprotonation extent, inducing a different adsorption mode. The step is found to be more reactive than the most basic BaO regular surface, in agreement with experimental observations on glycerol. The implications of these aspects in chemical reactivity are discussed.

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1. Introduction

Polyhydric alcohols (polyols) are regarded as potential green energy platform molecules in biorefinery schemes [1]. They are obtained from sugars or sugar alcohols as by-product in the biodiesel production and find a large number of applications in the pharmaceutical, cosmetic or petroleum industries. In the last years an effort has been made to develop heterogeneous catalysts able to optimize the industrial transformation process. Alkaline earth oxides are an important class of materials with promising application in polyol conversion. They are inexpensive and easily accessible basic catalysts with application in a variety of chemical transformations including isomerization, carbon–carbon and carbon–oxygen bond formation, and hydrogen transfer reactions [2].

Recently, alkaline earth basic homogeneous catalysts have successfully been used for the etherification of glycerol (CH_2OH–CHOH–CH_2OH) [3]. In that work, MgO, CaO, SrO and BaO materials are used as solid catalysts in the synthesis of di-, tri- and/or poly-glycerol, of importance as polymer additives (lubricants, plasticizers, emulsifiers, stabilizers and dispersants). Glycerol conversion is found to increase with increasing catalyst basicity. Furthermore,

Lewis acidity seems also to play an important role since differently prepared CaO materials show different glycerol etherification activity, which even may surpass that of BaO. On the other hand, ethylene glycol (CH_2OH–CH_2OH or 1,2-ethanediol) transesterification reactions lead to esters with superior lubricant properties [4]. The advantage in the use of alkaline earth basic catalysts for this reaction comes from the fact that the alkoxides obtained are insoluble in organic solvents, thus easily separated. In both etherification and (trans)esterification reactions, alkoxy species are key intermediates. It is thus of primary importance the understanding of the first stage in the mechanism, which is the alcohol interaction with the catalyst. The present paper aims at providing fundamental knowledge on the interaction of a simple diol with a basic solid surface by means of *ab initio* calculations. The ethylene glycol molecule and its interaction with basic solid catalysts MO (M = Mg, Ca, Sr and Ba) are modeled by periodic density functional theory (DFT). The geometry, strength of adsorption and deprotonation extent of the molecule will be analyzed as a function of the substrate basicity. Moreover, the role of surface defects will be studied in the case of CaO. The implications of the above mentioned aspects in reactivity are discussed.

2. Computational methods and models

Total energy calculations were carried out with the periodic *ab initio* code VASP [5,6]. The PW91 functional was used together with

Table 1
Selected geometrical parameters used in the DFT calculations for different alkaline earth metal oxides with rocksalt bulk structure. a: cell parameter, $d_{M–M}$: the shortest distance between two metal sites.

	MgO	CaO	SrO	BaO
Bulk				
a calculated (Å)	4.25	4.82	5.20	5.60
a experimental (Å)	4.21	4.80	5.20	5.52
(0 0 1) Plane				
$\sqrt{2}a$ (Å)	6.01	6.82	7.35	7.92
$d_{M–M}$ (Å)	3.00	3.41	3.67	3.96
$\sqrt{2} \times \sqrt{2}$ area (Å^2)	36.15	46.49	54.00	62.69

a plane wave basis set (cutoff 400 eV). The core electrons were replaced by PAW generated pseudopotentials [7,8], as in Ref. [9]. This methodology was tested for the bulk rocksalt structures leading to excellent agreement with experimental results, as can be seen in Table 1.

The regular surfaces have been modelled by cutting the optimized bulk structure through the most stable (0 0 1) plane. The CaO stepped surface is modelled by a (5 0 1) terminated slab. A five layer thick slab was used, the two bottom layers being fixed to the bulk optimized positions, the rest being allowed to relax. A vacuum of at least 10 Å prevents interaction between successive slabs. The distance between k-points in the reciprocal space was ~0.02 Å^{-1}. A $\sqrt{2} \times \sqrt{2}$ R45 unit cell was used for the adsorption systems on the regular surfaces; one ethylene glycol molecule is computed per unit cell. The adsorption energy is calculated as the energy of the molecule plus the substrate minus the interaction complex, and is positive for an exothermic adsorption. This scheme has been employed for a similar system (glycerol etherification on alkaline earth oxides) in good agreement with experimental results [3,9]. Implications of the sites studied in catalytic reactivity are discussed below. The extent of deprotonation of ethylene glycol is considered – note that "protonated" is used in the text to denote the presence of $O_{gly}H$ groups (not $O_{gly}H_2^+$), in contrast to "deprotonated" which denotes O_{gly}^- groups.

3. Results

3.1. Ethylene glycol adsorption on MO (M = Mg, Ca, Sr and Ba) (0 0 1) surfaces

The interaction of one ethylene glycol molecule on the $\sqrt{2} \times \sqrt{2}$ R45 unit cell of the different substrates implies a coverage of one molecule per four surface metal (or oxygen) sites. Different orientations of the molecule (perpendicular or parallel to the surface, on top of the metal sites or bridging two sites) have been explored for each substrate. Deprotonation of one or two alcohol groups has been considered following the reaction:

$$R–OH \rightarrow R–O^- + H^+ \tag{1}$$

Fig. 1 shows the most favorable adsorption modes obtained from the calculation, Table 2 summarizes the main results. For all the substrates ethylene glycol adsorbs parallel to the surface, the
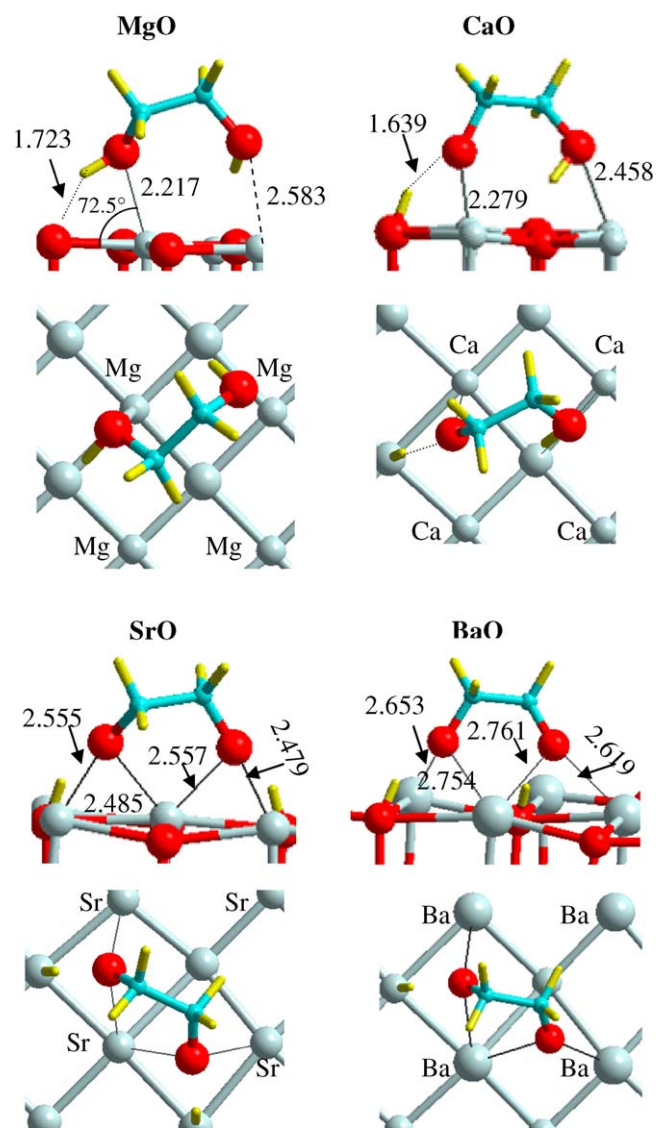

Fig. 1. The most stable adsorption modes for glycol interaction with MO (0 0 1) surfaces, top and side views. Selected distances in Å, angles in degrees.

alcohol groups in interaction with the surface. On MgO the molecule OH groups are located on quasi-top positions of the surface Mg sites. The molecule is completely protonated and the alcohol groups bind to the surface by hydrogen bonds. The $M–O_{gly}$ distances are in the range 2.2–2.5 Å. On the CaO surface the molecule lies on bridging positions between two surface Ca atoms. It is partially deprotonated forming an alkoxide $Ca–OCH_2CH_2OH$ with a Ca–O distance of 2.279 Å. On SrO the molecule is located in bridging positions. It completely deprotonates forming two alkoxide $Sr–OCH_2$ groups bridging two Sr surface sites each one. The $Sr–O_{gly}$ distances are around 2.5 Å. On BaO a similar picture is

Table 2
Coverage θ, shortest distance between two adsorbed species in two neighboring cells d(gly–gly), and adsorption energy E_{ads} obtained for all the metal oxide surfaces studied, positive values indicate exothermicity. The extent of deprotonation of the ethylene glycol molecule in the most favorable mode is reported (protonated means $O_{gly}H$ group, deprotonated O_{gly}^- group), together with the average $M–O_{gly}$ bond distance d($M–O_{gly}$).

	MgO	CaO	SrO	BaO	CaO step
θ (mol/nm^2)	2.77	2.15	1.85	1.60	0.84
d(gly–gly) (Å)	3.25	4.03	4.67	6.00	6.75
E_{ads} (eV)	0.77	1.34	1.66	2.55	2.73
Glycol protonation	Fully protonated	Partially protonated	Deprotonated	Deprotonated	Deprotonated
d($M–O_{gly}$) (Å)	2.2–2.5	2.3–2.5	2.5–2.6	2.6–2.8	2.3–2.5