Chemistry of sulfur oxides on transition metal surfaces: BOC-MP analysis

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Abstract

The bond order conservation-Morse potential (BOC-MP) method proved to be versatile and useful in analyzing chemisorption and reactivity on transition metal surfaces [1–3]. Most recently, we have applied the BOC-MP method to analyze surface chemistry of sulfur oxides on the Cu and Ni group metals [4,5]. We have calculated the reaction energetics (heats of adsorption, reaction enthalpies and intrinsic activation barriers) of the decomposition and oxidation of sulfur dioxide on fcc(111) surfaces of Cu, Ag, Au, Ni, Pd and Pt. The accuracy of the BOC-MP heats of adsorption has been verified by high quality (RECP-HF-MP2) ab initio calculations of the heats of SO_x adsorption ($x = 1, 2, 3, 4$) on Ag and Pd surfaces, which also clarified SO_x coordination modes. The BOC-MP analysis was made for low coverages without considering diffusional effects. The major model projections are: (1) The dissociation $SO_2 \to SO + O$ is unfavorable on all the metals considered; contrary to the common assumption, SO is unlikely to be a product of SO_2 dissociation. Also, on the Pt, Pd, Ni and Cu surfaces, SO is unstable. (2) The SO_2 dissociation is possible as $SO_2 \to S + O + O$, showing distinct periodic trends. It is feasible on Cu and particularly on Ni. (3) In the presence of carbon monoxide, the dissociation $SO_2 + CO \to S + O + CO_2$ may occur on all the metals examined. (4) The oxidation of SO_2 to SO_3 may be achieved with various-oxygen sources (e.g. O, O_2, H_2O_2 and NO) on Au, Ag, Pt and Pd surfaces. (5) Although adsorbed SO_3 may be readily obtained, it may be impossible to desorb SO_3 intact at low coverages because SO_3 will decompose to $SO_2 + O$ before desorption. (6) At elevated temperatures, the most stable of adsorbed sulfur oxides appears to be tetraoxide. As shown by Sellers et al. [6], its state is ionic and close to sulfate.

The relevant experimental data are discussed. Most of the model projections are in agreement with experiment. However, we suggest the reinterpretation of some of the reported experimental results and delineate model predictions to be verified in the future.

Keywords: Sulfur oxides; Copper; Silver; Gold; Nickel; Palladium; Platinum

1. Introduction

On a molecular level mechanisms of surface reactions comprising heterogeneous catalytic processes are poorly understood. Knowledge of the mechanistic details is critical to control surface reactions, but, it is far from clear how to obtain detailed information from experiment. It seems that computational science holds more promise of gaining reliable mechanistic information about catalytic events on metal surfaces.

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In principle, there are a number of theoretical approaches available, both quantum and classical mechanical, which can be used to model or simulate reactions on metal surfaces. We have reviewed the state of affairs of working theoretical approaches to surface chemistry and heterogeneous catalysis elsewhere [7]. Here we will only stress that the general problem is the lack of adequate (accurate enough for a given task) potential energy functions which cannot be compensated by sheer computer power. For example, quantum dynamics, classical dynamics and methods that combine them, involve solving equations that describe the time evolution of the system [8]. These time-dependent differential equations require the knowledge of a potential energy function, and, we are still not to the point that high quality potential energy functions for reactions on metal surfaces involving polyatomic reactants and products can be routinely computed with ab initio methods.

Statistical methods, including Monte Carlo, have been applied to the description of surface phenomena [9]. When used to describe processes involving thermal equilibrium these statistical methods are applications of Boltzmann statistics, and, knowledge of the energies of many system configurations is required, which again is determined by the accuracy of the potential energy function. Furthermore, for the simulation of time-dependent phenomena, such as chemical reactions, the energy barriers between system configurations are also needed [9]. Like the dynamics methods mentioned above, statistical methods have been applied to reacting systems involving diatomic adsorbates [9], and, ultimately they are limited by the lack of adequate potential energy functions.

The only theoretical method that has been applied to large and chemically interesting systems of reactions on metal surfaces is the bond order conservation-Morse potential (BOC-MP) method [1–3]. The BOC-MP method has been employed in the analysis of complex reaction mechanisms such as the direct conversion of methane to methanol [10] and the syngas

methane conversion [11], the hydrogen peroxide synthesis [12], the ammonia synthesis [13], CO hydrogenation [14], Fischer–Tropsch synthesis [15], the chemistry of nitrogen oxides [16], and allyl chemistry on metal surfaces [17]. These reaction mechanisms analyzed via the BOC-MP method are composed of a few tens of reactions up to two hundred. The method gains great efficacy by directly calculating surface reaction energetics and by not relying on equations of motion [1–3]. In a forthcoming review [7], we discuss in detail the abilities and limitations of the method, which will be known by a new name, including predictions of geometry parameters of adsorbed molecules and transition states.

In this work we have applied the BOC-MP method to the chemistry of sulfur oxides on the Cu and Ni group metals. Interest in the chemistry of sulfur oxides, particularly SO_2, has grown, in large part, from their roles as air pollutants and components of industrial processes [18,19]. Experimental studies have been conducted on all the metals of the Cu and Ni groups [20–42] employing a variety of experimental techniques. In particular, the periodic trends in SO_2 dissociation reported in the experimental literature are: (a) SO_2 dissociation does not occur on Ag or Au surfaces [22,26,28,30,41,42]; (b) SO_2 dissociation occurs to a small extent on some Pt and Pd surfaces [24,25,29,32–34,40]; (c) SO_2 dissociates completely on Ni(110) at low coverages [31,39]. On Cu(111) the slight dissociation of SO_2 has been attributed to the effect of defect sites [20–22]. On various metal surfaces, adsorbed SO, SO_3 and SO_4 have been proposed as intermediates and decomposition products, where the ionic states $O-SO_x$ are open to discussion [24,25,33,34,41,42]. Reports of SO and SO_4 desorption do not exist in the literature, and only on Pt(111) at high oxygen coverage was some desorption of SO_3 reported [33]. The fact that SO_3, a stable molecule in the gas phase, does not usually desorb from the copper and nickel group metals has been interpreted as evidence that adsorbed SO_3 is likely to be

sulfite [41]. Interpretation of these diverse experimental data is far from convincing so that a theoretical study of sulfur oxide chemistry may contribute to a coherent understanding.

2. Major features of the BOC-MP method

The BOC-MP method [1–3] is an algebraic, predictive technique that employs atomic heats of adsorption and gas phase molecular bond energies to predict molecular heats of adsorption and activation barriers for Langmuir–Hinshelwood reactions on metal surfaces. An attractive aspect of the method is the fact that all the parameters employed are observable thermodynamic quantities and are, therefore, physically well defined quantities. Moreover, the use of observable quantities automatically accounts for effects of numerous contributions to those quantities, for example, explicit geometries of adsorbate and metal atoms including surface relaxation, that add to the computational complexity when other methods are employed, for example, ab initio electronic structure theory. The method assumes that the interactions between surface metal atoms and adsorbate atoms are quasispherical (depend on distance only) which seems to be most justifiable for surfaces in which the surface metal atoms have high coordination numbers.

The energy functions employed in the BOC-MP method are polynomial expressions that are rigorously reduced, without loss of generality, to quadratic functionals of a variable, $x = x(r)$, which is characteristic of the two center atom–atom interaction, namely $E = Q(x^2 - 2x)$, and, r is the internuclear distance. The form of this functional is uniquely determined by two requirements: (1) it possesses a single minimum which occurs at $E = -Q$ when $x = 1$; and, (2) $E \to 0$ as $x \to 0$. The constraints that the $x(r)$ must satisfy are: (a) it is everywhere positive for finite internuclear distance, r, and approaches zero asymptotically as the internuclear distance increases without limit; and, (b) r and $x(r)$

map uniquely onto one another so that a particular value of $x(r)$ implies a unique value of r and vice versa. Because the wavefunctions of atom–atom interacting systems have exponential character, a general expression for $x(r)$ is: $x(r) = \sum_i c_i \exp\{-(r - r_{0,i})/a_i\}$ where the summation is infinite in principle. By varying the parameters in this function, there is enough flexibility in the energy expression to fit any physically reasonable two body potential that conforms to the imposed requirements. When there is only one term in the summation, $x(r) = \exp\{-(r - r_0)/a\}$, and $E = Q(x^2 - 2x)$ is a Morse potential. Thus the Morse potential is a first approximation to the accurate interaction potential it represents. The explicit reference to the Morse potential in the name of the BOC-MP method is actually an unnecessary limitation that obscures the fact that the interaction potential employed is of a general nature. We discussed these issues in detail elsewhere ([3,7]) and, in the interest of clarity suggested to replace the reference to the Morse potential in the name of the method.

Along a molecular chemisorption path, the total system bond order, composed of additive two center contributions, is considered to be constant and normalized to unity up to the dissociation point, after which each fragment (atom) becomes an independent system subject to the BOC constraints. The principle of the conservation of bond order to unity has been verified with ab initio calculations for linear, three center (gas phase) reacting systems [43–46] and for several diatomic reactions on metal surfaces [47]. The activation barriers are obtained through an interpolation process [1–3].

The BOC-MP method has a proven track record with regard to the quality of its projections. Numerous calculations using the BOC-MP method have shown that heats of adsorption for diatomic and polyatomic adsorbates are usually in agreement with results of careful experiments to within 2 or 3 kcal/mol [1–7,10–17]. We are unaware of a case in which the BOC-MP method fails to make adequate projections of heats of

adsorption at low coverage and even at higher coverage when lateral interactions and coverage effects are taken into account. There are fewer experimental activation barrier results available with which to compare; however, the BOC-MP method has made coherent projections of surface chemistry in agreement with experiment which points to the reliability of the projections of reaction activation barriers as well [1–7,10–17].

3. Results

3.1. Heats of chemisorption of sulfur oxides

For the details of the calculations of heats of adsorption and activation barriers and corresponding formula the reader is referred to Refs. [4,5]. The low coverage heats of adsorption of SO, SO_2, and SO_3 on the (111) surfaces of the copper and nickel group metals are given in Table 1. These data correspond to SO chemisorbed parallel to the plane of the surface, SO_2 and SO_3 di-coordinated via two oxygens. BOC-MP and high quality ab initio calculations [4,5] have determined these chemisorption modes and binding sites to be reasonable candidates for the preferred binding situations. On these metals the heat of adsorption of SO, from 9 to 17 kcal/mol, is roughly half that of O_2 and SO_3. The heat of adsorption of SO_3 is only marginally larger than that of SO_2. These heats of adsorption are employed in our BOC-MP

Table 1
Calculated heats of adsorption, Q, in preferred di-coordinated bridging sites for SO, SO_2 and SO_3 on fcc(111) surfaces [a]

Metal	Q_{SO}	Q_{SO_2}	Q_{SO_3}
Cu	14	30	33
Ag	9	20	21
Au	9	18	19
Ni	17	36	39
Pd	12	23	25
Pt	11	22	24

[a] SO_2 and SO_3 are di-coordinated via two oxygens. Energies are in kcal/mol.

Table 2
Calculated heats of adsorption, Q, reaction enthalpies, ΔH, and activation barriers for the asymmetric, E_a^*, and symmetric, E_s^*, dissociation paths for SO_2 on fcc(111) surfaces [a]

Metal	Q	ΔH_a	E_a^*	ΔH_s	E_s^*
Cu	30	+45	45	−7	27
Ag	20	+63	63	+38	38
Au	18	+66	66	+44	48
Ni	36	+36	36	−50	13
Pd	23	+56	56	+9	35
Pt	22	+58	58	+16	38

[a] Energies are in kcal/mol.

determinations of the activation barriers of the surface reactions studied.

3.2. SO_2 dissociation

Much experimental work [20–42] has dealt with the dissociation of SO_2 on copper and nickel group metals and the identities of the dissociation products. The usual proposed dissociation path, which we refer to as the asymmetric path, is:

$$SO_2 \rightarrow SO + O \qquad (1)$$

In addition to this we also considered the symmetric dissociation path:

$$SO_2 \rightarrow S + O + O \qquad (2)$$

Both dissociation paths are elementary reaction steps which can be thought of as being initiated by the asymmetric and symmetric stretching modes, respectively. The symmetric path, producing adsorbed atomic sulfur and oxygen, involves the simultaneous breaking of both S–O bonds, while the asymmetric path, which produces surface adsorbed SO and atomic oxygen, involves the cleavage of one S–O bond.

The heats of adsorption of SO_2, reaction enthalpies and activation barriers for both dissociation paths on the copper and nickel group metals are given in Table 2. The asymmetric dissociation path is highly endothermic. The activation barriers for the asymmetric dissociation path are too high for this reaction to occur on all the metals considered. The symmetric

dissociation path, producing atomic sulfur and oxygen is slightly exothermic on Cu and highly exothermic on Ni. In order for a surface reaction to take place, the barrier to reaction should be lower than the desorption barriers of the reactants. This is clearly the case only for the symmetric dissociation path of SO_2 on nickel in which the barrier to dissociation is 13 kcal/mol and the SO_2 desorption barrier is 36 kcal/mol. For Cu, the dissociation barrier along the symmetric path is about the same as the reactant desorption barrier. The reaction enthalpies and activation barriers show the periodic trends of increasing as one goes down and to the right in the periodic table.

We also considered the possibility that SO_2 dissociation might be enhanced by the presence of coadsorbates. An important coadsorbate in this regard is CO, since it is a common surface contaminant. Table 3 contains the reaction enthalpies, forward and reverse activation barriers for the reaction:

$$SO_2 + CO \rightarrow S + O + CO_2 \qquad (3)$$
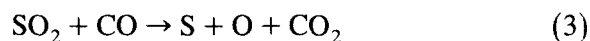
This reaction results by allowing CO to interact with the SO_2 adsorbate as it proceeds along the symmetric dissociation path. The projections of the BOC-MP method are that this reaction is exothermic on all the metals considered except gold and silver and only slightly endothermic on these two metals. The reaction is projected to occur with zero activation energy on all but gold and silver, and, the barriers on Ag and Au are small.

Table 3
Calculated enthalpies of reaction, ΔH, and forward, E_f^*, and reverse, E_r^*, activation barriers for the reaction on fcc(111) surfaces: $SO_2 + CO \rightarrow CO_2 + S + O$ [a]

Metal	ΔH	E_f^*	E_r^*
Cu	−21	0	21
Ag	+9	9	0
AAu	+9	9	0
Ni	−39	0	39
Pd	−8	0	8
Pt	−6	0	6

[a] Energies are in kcal/mol.

Table 4
Calculated heats of adsorption, Q, reaction enthalpies, ΔH, and barriers to dissociation, E^*, of SO on fcc(111) surfaces [a]

Metal	Q	ΔH	E^*
Cu	14	−52	0
Ag	9	−24	8
Au	9	−21	9
Ni	17	−85	0
Pd	12	−45	0
Pt	11	−41	2

[a] Energies are in kcal/mol.

3.3. Other reaction products

3.3.1. SO as a decomposition product and surface adsorbate

Although SO_2 is the only sulfur oxide that has been observed to desorb at low coverages from any metal surface, other sulfur oxides, SO, SO_3^{2-} and SO_4^{2-}, have been proposed as surface adsorbed products resulting from the decomposition or oxidation of SO_2 [24,25,29,32–35,40]. Above we have shown that the results of the BOC-MP modeling disallow SO as a product of SO_2 dissociation. Table 4 contains the heats of adsorption of SO, enthalpies and activation energies for the dissociation of SO on the copper and nickel group metals. The BOC-MP method projects that SO should decompose without activation energy on Cu, Ni and Pd and with only small barriers on Ag, Au and Pt. The decompositions are all significantly exothermic. So, the BOC-MP results indicate that SO should not be formed from the decomposition of SO_2, and, even as a surface adsorbate independent of its source, SO should be thermodynamically unstable and decompose without barrier on Cu, Ni, and Pd.

3.3.2. Products of SO_2 oxidation

As indicated by the data presented in Table 5, SO_2 may be oxidized to SO_3 by several oxygen sources. Atomic and molecular oxygen, hydrogen peroxide and nitrogen monoxide are predicted to be efficient oxygen sources for the oxidation of SO_2 while CO, CO_2, SO_2, SO and

Table 5

Calculated enthalpies of oxidation, ΔH, and forward, E_f^*, and reverse, E_r^*, activation barriers for the reaction on fcc(111) surfaces: $SO_2 + OX \rightarrow SO_3 + X$ [a]

OX	Metal	ΔH	E_f^*	E_r^*
O	Cu	+17	20	3
	Ag	−5	5	10
	Au	−10	2	12
	Ni	+29	29	0
	Pd	+2	10	8
	Pt	+0	8	8
O_2	Cu	−54	0	54
	Ag	−36	0	36
	Au	−32	0	32
	Ni	−63	0	63
	Pd	−42	0	42
	Pt	−40	0	40
H_2O_2	Cu	−42	0	42
	Ag	−55	0	55
	Au	−41	0	41
	Ni	−55	0	55
	Pd	−41	0	41
	Pt	−39	0	39
NO	Cu	−24	1	25
	Ag	−14	2	16
	Au	−12	2	14
	Ni	−36	0	36
	Pd	−32	0	32
	Pt	−24	0	24
CO_2	Cu	+31	31	0
	Ag	+23	23	0
	Au	+25	25	0
	Ni	+18	18	0
	Pd	+20	20	0
	Pt	+22	22	0
CO	Cu	+67	67	0
	Ag	+49	49	0
	Au	+53	53	0
	Ni	+29	31	2
	Pd	+38	38	0
	Pt	+45	45	0
SO	Cu	−34	0	34
	Ag	−29	0	29
	Au	−31	0	31
	Ni	−56	0	56
	Pd	−43	0	43
	Pt	−41	0	41
OH	Cu	+32	32	0
	Ag	+20	20	0
	Au	+23	23	0
	Ni	+34	34	0
	Pd	+15	16	1
	Pt	+15	16	1

Table 5 (continued)

OX	Metal	ΔH	E_f^*	E_r^*
SO_2	Cu	+63	63	0
	Ag	+58	58	0
	Au	+56	56	0
	Ni	+65	65	0
	Pd	+58	58	0
	Pt	+58	58	0

[a] Energies are in kcal/mol.

OH should be inefficient at oxidizing SO_2 on the metals examined.

The reverse of the oxidation reaction of SO_2 to SO_3 with atomic oxygen as the oxygen source is just the decomposition of SO_3 to SO_2 and O. The barriers for this reaction are found in Table 5. Comparing these barriers to decomposition of SO_3 to the barriers to desorption of SO_3 (Table 1) reveals that in all cases SO_3 is projected to decompose at low coverages before it could desorb.

The nature of SO_3 and SO_4 adsorbed specie, in particular the issue of ionic character of the adsorbed compounds, has been discussed in the literature [27,41,42]. Remember that the chemisorbed state of an adsorbate, X, is the same regardless of what was the initial state, neutral X or ionic $X^{m\pm}$ [6]. Our high quality ab initio calculations (RECP Hartree–Fock + electron correlation) on large Ag(111) clusters [48] have shown that $SO_3^=$ loses most of its ionic electrons to the metal bulk and becomes basically a neutral SO_3 entity, but, $SO_4^=$ remains essentially as sulfate with the binding energy up to 160 kcal/mol. Thus, sulfite should be only a transient surface specie and not a relevant participant in the chemistry of sulfur oxides on these metal surfaces. However, adsorbed SO_4 as sulfate should be stable at elevated temperatures and, as thermodynamic considerations indicate, should decompose before it desorbs [48].

3.4. Conclusions from modeling

The picture that arises from the BOC-MP and ab initio modeling is: (a) the asymmetric disso-

ciation of SO_2 to give $SO + O$ is unfavorable on all the metals examined; (b) the symmetric dissociation of SO_2 giving atomic sulfur and oxygen shows distinct periodic trends and is feasible on Ni and to some extent Cu; (c) carbon monoxide may stimulate the symmetric decomposition of SO_2 on all the metals examined giving atomic sulfur as a decomposition product; (d) SO should be thermodynamically unstable on the copper and nickel group metals and decompose without barrier on Pd, Ni and Cu; (e) adsorbed SO_2 may be converted to adsorbed SO_3 by O, O_2, H_2O_2 and NO as oxygen sources on all the metals studied; (f) the barrier to SO_3 desorption is significantly greater than the decomposition barrier and so it may not be possible to desorb SO_3 at low coverages; (g) sulfite should lose its anion electrons to the metal surface while sulfate should remain a stable surface adsorbate; (h) at elevated temperatures exceeding the desorption temperature of SO_2, the most stable adsorbed sulfur oxide should be sulfate; the decomposition of SO_4^- to SO_2 and O should occur before sulfate desorption.

4. Comparison with experiment and discussion

4.1. Sulfur oxide desorption

To date the only oxide of sulfur that has been observed to desorb at low coverage from surfaces of Cu and Ni group metals is SO_2 [20–42]. This is precisely the picture we obtain from our modeling results. The BOC-MP method projects that, while SO_3 may form by oxidation of SO_2 on the surface, it has decomposition barriers that are less than the desorption barriers, and, therefore should decompose before desorption. The BOC-MP method also projects that SO cannot be formed by dissociation of SO_2 on the Cu and Ni group metals, not to mention that the dissociation barriers for SO on Pt, Pd, Ni and Cu are smaller than the desorption barriers. On

gold and silver the barrier to SO decomposition is nearly the same as the desorption barrier and one might expect that SO could be desorbed immediately after deposition from the gas phase, however, to our knowledge this experiment has not been done. Our ab initio and thermodynamic calculations [4,5,48] indicate that SO_4 exists on metal surfaces as sulfate and, although it should be stable at elevated temperatures [48], it should decompose to SO_2 and oxygen before the anion desorbs.

4.2. SO_2 decomposition

SO_2 is desorbed with no evidence of decomposition from all silver surfaces [22,26,28,30,41,42]. At low coverages SO_2 decomposes completely upon heating on Ni(110) [31] with no evidence of SO as a decomposition product. Sulfur dioxide was found to be molecularly adsorbed on Ni(111), Ni(100) and Ni (110) at 150 K [37–39], which places the barrier to decomposition greater than 10–12 kcal/mol. These observations are consistent with our modeling projections, namely that SO_2 decomposition is not feasible on silver surfaces, but, is feasible on Ni surfaces with a barrier of 13 kcal/mol.

On Pt and Pd surfaces a fraction of the adsorbed SO_2 has been observed to decompose [24,25,29,32–34,40], although the BOC-MP method projects that SO_2 should not decompose on Pt or Pd (Table 2). We believe that this decomposition is not intrinsic for Pt and Pd surfaces, but rather, results from some extraneous factors. In particular, the experimental techniques employed to study these systems, contaminant coadsorbates such as CO and surface defect sites might be responsible for the observed marginal decomposition of SO_2 on Pt and Pd. Wassmuth et al. [21] have presented convincing evidence that these sources are indeed responsible for the similar marginal dissociation of SO_2 on Cu(111). The experimental evidence for SO_2 dissociation on Pd and Pt surfaces to date involves the use of experimen-

tal techniques such as LEED and AES that are known to stimulate the decomposition of SO_2 [22]. Our modeling projects, in agreement with observations on Pt(111) [24,25] and Pt(100) [36], that CO will stimulate the dissociation of SO_2.

4.3. Identification of adsorbed sulfur oxides

The experimental identification of products of SO_2 decomposition and oxidation reactions on Cu and Ni group metal surfaces has been based mostly on assignments of electron energy loss features by comparisons of these vibrational data with known frequencies of ligand complexes of sulfur oxides [21,32,34,42]. There are several difficulties with this procedure. First of all, there are surface binding situations that have no analogs with those of ligand complexes. Furthermore, there are usually several possible chemisorption modes and binding sites available to the polyatomic adsorbates, and, indeed some experimental observations have pointed to changes in coordination modes [41]. However, there is presently no information available regarding the changes in SO_2 vibrational spectra that occur when the admolecule undergoes a change in chemisorption mode or binding site. There is a significant danger that different sulfur oxides are erroneously postulated as surface specie to explain shifts in vibrational spectra that may be in fact due to SO_2 in different binding sites or coordination modes. A more detailed discussion of the problems associated with these assignments has been given elsewhere [4,5].

Sulfur monoxide has been proposed at elevated temperatures as an adsorbed product of the decomposition of SO_2 on Pt and Pd surfaces [24,25,32,34,40], although identification of SO was characterized as 'not unambiguous' on Pd(100) [32] and no identification at all was made for Pt(111) and Pd(111) [24,25,40]. SO_3 has been reported to exist on silver surfaces [41,42] and SO_4 has been proposed to exist on Pt and Pd surfaces at elevated temperatures [32,34]. As explained above, we believe that the

experimental evidence for the formation of surface adsorbed SO and the presence of SO_3 at elevated temperatures is not definitive and should be reconsidered. Our large ab initio calculations indicate that sulfite in the low coverage limit converts to practically neutral SO_3 upon adsorption, and, sulfate essentially retains its dianioinic character once adsorbed [48]. This together with thermodynamic considerations [5,6] lead to the conclusion that adsorbed $SO_4^=$ should be stable to elevated temperatures and decompose to SO_2 and oxygen before desorption. We believe that if a sulfur oxide species is observed at elevated temperatures, it should be sulfate.

5. Concluding remarks

Our model projections regarding the chemistry of sulfur oxides on surfaces of the Cu and Ni group metals are: (1) The dissociation of $SO_2 \rightarrow SO + O$ is unfavorable on the metals studied, but, the dissociation $SO_2 \rightarrow S + O + O$ is feasible on Cu and particularly on Ni. (2) CO may stimulate SO_2 decomposition on the metals examined. (3) SO is unstable on Pd, Pt, Ni and Cu surfaces. (4) The oxidation of SO_2 to SO_3 may be achieved with O, O_2, H_2O_2 and NO as oxygen sources on Ag, Au, Pd and Pt surfaces. (5) Although adsorbed SO_3 may be readily obtained, it may be impossible to desorb SO_3 intact at low coverages because SO_3 will decompose to $SO_2 + O$ before desorption. (6) sulfur oxide specie that withstand elevated temperatures above the desorption temperature of SO_2 should be sulfate.

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