An Insight into Electrostatic Field Effects on SO₃ Adsorption by CaO with CO₂, SO₂ and H₂O: A DFT Approach

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ABSTRACT

Because of the compulsory installation of electrostatic precipitators in coal-fired power plants, SO₃ and particles in flue gas inevitably pass through areas with electric field and electric charge distributed. CaO is the highest alkaline content in fly ash and has strong interactions with SO₃. Therefore, it is important to understand the effects of the electric field on the binding energies of SO₃ and CaO. Density functional theory calculations were applied to examine the electrostatic field dependence of SO₃ adsorption on the CaO(100) surface. The energetic, geometric and electronic nature of the modeled systems was analyzed. Trends of the adsorption energy variation in a positive or negative electrostatic field presented great differences. When the electrostatic field was small, it was observed that the required adsorption energy was reduced regardless of the positive or negative electrostatic field. With increased electrostatic field strength, the adsorption energy showed an increasing trend in a positive field, while the adsorption energy decreased in a negative field. The positive field enhanced the charge density changes of the surface O across the Ca around the O_{CaO}, while the negative field enhanced the change of the charge density of the Ca below the O_{CaO}. The SO₄²⁻-like structure accumulated electrons as a unit and the charge transfer of the SO₄²⁻ increased with the incremental adsorption energy in a linear relationship. On the H pre-adsorbed surface, the total increment was much smaller than in previous cases in a positive field, and the total variation was negligible in a negative field.

Keywords: SO₃; CaO; Electrostatic field; Adsorption; Density functional theory.

INTRODUCTION

The coal combustion process has been counted as the most important source of atmospheric pollutant emissions, including particulate matter (PM), SO₂, NO_x and various heavy metals (Zhao *et al.*, 2010; Czarnowska and Frangopoulos, 2012). To remove those harmful pollutants, NH₃ selective catalytic reduction (NH₃-SCR), electrostatic precipitators (ESPs) and wet flue gas desulfurization (WFGD) systems have been applied and proven effective (Chang *et al.*, 2015; Hu *et al.*, 2017; Liu *et al.*, 2017; Song *et al.*, 2018). SO₃, generated from SO₂ oxidation, is more harmful to the environment than SO₂ because it can hardly be removed by the above removal equipment and can transform into sulfate aerosols and secondary sulfate particles in WFGD systems and out of the power station flues (Bin *et al.*, 2017; Liu *et al.*, 2018b). When the flue gas has passed through the WFGD, the weight percentage of S and Ca increases significantly,

most of which is contained in fine particles. The increase of Ca is ~10%, generated from CaO, CaCO₃ and CaSO₄ fine particles. For S, the increase can be as high as 30%, resulting from CaSO₄ fine particles, acid dew phenomena and physical chemistry interaction between SO₃, SO₂ and fine particles (Zhou, 2011).

In flue gas, SO₃ is generated predominantly through three processes: combustion, catalytic oxidation of SO₂ by fly ash or the NH₃-SCR system (Wang *et al.*, 2011; Fleig *et al.*, 2012; Du *et al.*, 2018; Wang *et al.*, 2018). By fly ash, SO₃ can also be captured and removed via fly ash collection (Spörl *et al.*, 2014; Zhao *et al.*, 2018). CaO, one of the main components of fly ash, has alkaline properties, by which it can adsorb SO₃ (Wang *et al.*, 2012). The capture of SO₃ by CaO is even better than that of SO₂ (Marier and Dibbs, 1974). Wang *et al.* (2011) have tested the capture efficiency of SO₃ by CaO at 250–400°C and found the efficiency can achieve 80% at a proper equivalence ratio and flue gas residence time. Galloway *et al.* (2015) have found that SO₃ interacts with the alkali or alkaline metal oxides through the formation of sulfate structures.

In ESP and other fine-particle removal equipment, such as wet electrostatic precipitators (WESPs) and wet electro-scrubbers (WES), particles in flue gas are in areas with

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electric field and distributed electric charge. In research of molecular adsorption on metal oxide surfaces, noble metal surfaces or other materials with active surfaces, an externally applied electric field can enhance bonding interaction by dipole moment, defect formulation or electrostatic force increase, etc. (Sun *et al.*, 2010; Lv *et al.*, 2011; Youssef *et al.*, 2017) Also, an externally applied electric field can be a promising means to make changes in adsorption enthalpy. Most studies have explored effects of the electrostatic field by means of theoretical calculations, especially *ab initio* simulations. In a study of hydrogen storage, the capacity of hydrogen adsorption on mesoporous nickel and magnesium oxides is significantly enhanced by the electrostatic field, 37.5% for nickel oxide and 25% for magnesium oxide (Sun *et al.*, 2010). Wang *et al.* (2017) have found that interactions in dopamine-graphene systems are sensitive to applied electrostatic field. Applying an electrostatic field in an adsorbate-surface system leads to lengthening of adsorbate bonds and an increase of the electronic charge transferred from the surface to the adsorbate (Koper and Santen, 1999). Ao *et al.* (2010) have studied the correlation of the applied electrostatic field and CO adsorption/desorption behavior on Al-doped grapheme and they found that an electrostatic field at the normal direction to graphene surfaces strengthens CO adsorption, while adsorption is reduced when an electrostatic field is present at an opposite direction. Yue *et al.* (2013) have applied a perpendicular electrostatic field when investigating the adsorption of various gas molecules on monolayer MoS₂, demonstrating that the application of a perpendicular electrostatic field can consistently modify the charge transfer between the adsorbed molecule and the MoS₂ substrate. The above calculations and simulations indicated that molecule adsorption is sensitive to the applied electrostatic potential.

Experimental study in this area is not that easy to implement, but there are several feasible approaches. Zhang *et al.* (2013) have investigated the performance of hydrogen adsorption on AC/TiO₂ nanoparticles in the presence of an electric potential by grounding the upper end of the sample holder and connecting the lower end to a high voltage DC power supply. The results showed that the adsorption capacity could be enhanced by introducing an electric potential and the enhancement increased with increased amounts of TiO₂ nanoparticles. Htwe *et al.* (2016; 2018) have evaluated the amounts of adsorbed protein as a function of applied surface potential and found that a negative polarization of the metal oxide surface tends to restrain protein adsorption, whereas it is strongly enhanced when the surface potential range is above a certain value.

As SO₃ and particles in flue gas will inevitably pass through areas with electric field and electric charge distributed, there might be enhancement or suppression of interactions between SO₃ and particle components. In this study, the focus was on CaO, which is the highest alkaline content in fly ash that has strong interactions with SO₃. If electric field or surface electric charge could increase the binding energy of SO₃ and CaO, new approaches for SO₃ control might be proposed. Therefore, the goal was to examine the effects of electrostatic field on SO₃ adsorption on CaO through density functional theory (DFT) calculations.

COMPUTATIONAL METHODOLOGY

Plane-wave density functional theory calculations were performed in the Vienna Ab-initio Simulation Package (VASP) version 5.2 (Kresse and Furthmüller, 1996a, b). The electron exchange-correlation functional was treated with the generalized gradient approximation (GGA-PBE) (Perdew and Wang, 1992; Perdew *et al.*, 1992) with the projector-augmented wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999). The 2s²2p⁴, 3s²3p⁴ and 3s²3p⁶4s² electrons were included explicitly as the valence for the O, S and Ca atoms, respectively, and the remaining electrons were kept fixed as core states.

The supercell model was built from the cubic CaO unit cell with a lattice constant of $a = 4.84 \text{ \AA}$, which was obtained by calculation. For the surface model, the (100) surface was modeled using periodic slabs to characterize the SO₃-surface interactions, because it is the most common exposed surface of CaO. The slab model was a $p(2 \times 2)$ lateral cell with three atomic layers thick and a $15 \text{ \AA}$ vacuum gap in the direction perpendicular to the surface. The bottom three atomic layers were fixed, while the top two atomic layers were relaxed. Relaxation of the model was carried out until the maximum Hellmann-Feynman force was less than $0.03 \text{ eV/\AA}$. The calculations were carried out using the Brillouin zone sampled with $(3 \times 3 \times 1)$ Monkhorst-Pack mesh k -points grid with a cutoff energy of 520 eV and a Gaussian smearing of 0.1 eV. While perform calculation on unit cell, a Monkhorst-Pack of $(9 \times 9 \times 9)$ was employed. The external electrostatic field is applied by adding a dipole moment pointing perpendicular to the slab model. The topology of the CaO(100) system with electrostatic field is shown in Fig. 1. The arrows denote the positive direction of the electrostatic field.

The adsorption energies (E_{ads} , kJ/mol) were defined as:

$$E_{\text{ads}} = E_{\text{slab+SO}_3} - E_{\text{slab}} - E_{\text{SO}_3} \quad (1)$$

where $E_{\text{slab+SO}_3}$ and E_{slab} are the total energy of the systems with and without SO₃ adsorbed, respectively, and E_{SO_3} is the total energy of a SO₃ molecule in the gas phase (Liu *et al.*, 2018a). The minus sign in adsorption energy means it is an exothermic process, and the stability of the formed structure improves with absolute value of the adsorption energy.

Charge transfer between SO₃ and the surface is obtained *via* Bader analysis (Henkelman *et al.*, 2006; Tang *et al.*, 2009). Charge density difference (CDD, $\Delta\rho$, e/Å³) plots were also used to examine the charge transfer, which was calculated from the electron localization function (Becke and Edgecombe, 1990; Silvi and Savin, 1994) and obtained as:

$$\Delta\rho = \rho_{(\text{slab+SO}_3)} - \rho_{\text{slab}} - \rho_{\text{SO}_3} \quad (2)$$

In this equation, $\rho_{(\text{slab+SO}_3)}$ represents the charge density for the adsorbed system; while ρ_{slab} and ρ_{SO_3} indicate the charge density of the non-adsorbed subsystem and the SO₃ molecule.

Fig. 1. Topology of CaO unit cell and side view of CaO(100) system with electric field.

RESULTS AND DISCUSSION

Effects of Electrostatic Field on SO₃ Adsorption onto CaO

When SO₃ adsorbs onto a CaO(100) surface, it forms a structure parallel to the surface with the S binding on O_{slab}, as shown in Fig. S1. The adsorption energy of SO₃ on CaO surface in a zero electrostatic field agrees quite well with earlier DFT-generalized gradient approximation results (Galloway *et al.*, 2015). Fig. 2 shows the adsorption energy of SO₃ on the surface of CaO for various electrostatic field conditions. In areas where the electrostatic field is small, the required adsorption energy is observed to be reduced regardless of it being a positive or negative field, from $-321.9 \text{ kJ mol}^{-1}$ with no field to -318.4 and $-317.6 \text{ kJ mol}^{-1}$, respectively. Then, with increased electrostatic field with a positive direction, the adsorption energy shows an increasing trend; in the case of negative electrostatic field, the adsorption energy shows a decreasing trend. As the electrostatic field rises from $0.05 \text{ V/\AA}$ to $0.5 \text{ V/\AA}$ in a positive direction, the binding energy increase from $-318.4 \text{ kJ mol}^{-1}$ to $-357.6 \text{ kJ mol}^{-1}$. In the negative direction, it declines to $-287.0 \text{ kJ mol}^{-1}$ with a field of $0.5 \text{ V/\AA}$. The variation tendency of the adsorption energy with respect to the electrostatic field is in agreement with results in the study of other adsorbate-surface systems (Ao *et al.*, 2010; Yue *et al.*, 2013). The structural parameters for SO₃ adsorption on CaO surface are shown in the Table 1, Tables S1 and S2. While the electrostatic field is increasing in a positive direction, the bond length between S and O_{CaO} is becoming shorter; the bond angles of O_{SO3}-S-O_{SO3} first increases from 113.65° at 0 eV to 113.75° at 0.05 eV , and then decreases to 113.59° at 0.5 eV . The bond angles of O_{CaO}-S-O_{SO3} exhibits the opposite trend and the bond length is nearly invariable. When the electrostatic field is in a negative direction, there are also corresponding changes in structural parameters with adsorption energy.

Fig. 3 presents the local density of states (LDOS) plot of s- and p-orbitals of S, O_{SO3} and O_{CaO}. Because of the covalent

bonding between S and O, the orbital of S and O eventual reunified in several levels, around -10.03 , -7.99 , -7.28 , -4.85 , -4.14 , -2.63 , -2.10 eV , etc. at zero field. Similar DOS plots of S, O_{SO3} and O_{CaO} indicate that a SO₄²⁻-like structure has formed. It can be seen that the existence of the electrostatic field is observed to have no effect on the distribution of the orbital density, but shifted the energy of the orbital. When the adsorption energy increases, the orbit moves to a lower energy. The change is about 0.2 eV for a field of $0.5 \text{ V/\AA}$. The charge transfer of the SO₄²⁻-like structure in relation to the electrostatic field is illustrated in Fig. 4. It is found that, except in zero field, the charge transfer of the SO₄²⁻ increases with the electrostatic field intensity in the positive direction, whereas it tends to decrease once a reverse electrostatic field is applied. The variation of the charge transfer vs. electrostatic field was nearly linear. It is easy to conjecture that the charge transfer also increases with the increment of adsorption energy in a linear relationship, as shown in Fig. S2. This result also illustrates that the SO₄²⁻-like structure accumulates electrons as a unit.

Systems with CO₂ and SO₂ Adsorbed on CaO

When CO₂ is adsorbed on the surface at site 1 and site 2, the adsorption energy of SO₃ decreases to $-250.8 \text{ kJ mol}^{-1}$ and $-302.0 \text{ kJ mol}^{-1}$ at zero field, respectively. The adsorption of CO₂ is much weaker than SO₃, and the variation tendency of the adsorption energy with respect to the electrostatic field is similar to the results of SO₃ adsorbed, as shown in Fig. 4(a). When a small electrostatic field is applied in the case with CO₂ adsorbed, the extent of reduction in adsorption energy of SO₃ is much larger than the case without CO₂, about 7.35 – 9.23 kJ mol^{-1} (Figs. 5(b) and 5(c)). There is a difference of $54.50 \text{ kJ mol}^{-1}$ at site 1 and $48.23 \text{ kJ mol}^{-1}$ at site 2 between the field of 0.5 and $-0.5 \text{ V/\AA}$, which is smaller than the case without CO₂ adsorbed ($73.75 \text{ kJ mol}^{-1}$). The variation of the structural parameters is consistent with the adsorption energy.

Fig. 2. Adsorption energies of SO₃ on CaO(100) surface with electric field in or opposite the normal direction of the surface.

Table 1. Summary of the adsorption energies and structural parameters for SO₃ adsorption on CaO(100) surface with electric field.

Systems	Electrostatic field (V/Å)	E_{ads} (kJ mol ⁻¹)	$d\text{S-O}_{\text{CaO}}$ (Å)	$d\text{S-O}_{\text{SO}_3}$ (Å)	bond angles of O _{SO3} -S-O _{SO3} (°)	bond angles of O _{CaO} -S-O _{SO3} (°)
SO ₃ only	0.50	-357.6	1.59	1.47	113.59	104.71
	0	-321.9	1.60	1.47	113.65	104.32
	-0.50	-283.9	1.61	1.47	114.25	103.73
+CO ₂ site 1	0.5	-272.0	1.62	1.47	114.16	103.68
	0	-250.8	1.63	1.47	114.50	103.37
	-0.5	-217.5	1.64	1.47	115.19	102.68
+CO ₂ site 2	0.5	-321.3	1.60	1.47	113.28	103.80
	0	-302.0	1.60	1.47	113.62	103.48
	-0.5	-273.0	1.61	1.47	114.48	102.91
+SO ₂	0.5	-261.7	1.62	1.47	114.14	103.70
	0	-241.7	1.63	1.47	114.42	103.41
	-0.5	-211.4	1.64	1.47	115.10	102.80
+H	0.5	-305.1	1.60	1.47	113.52	105.65
	0	-295.8	1.60	1.47	113.65	105.49
	-0.5	-297.3	1.60	1.47	114.09	104.93
+OH	0.5	-344.0	1.59	1.47	113.22	105.94
	0	-318.0	1.60	1.47	113.56	105.76
	-0.5	-280.6	1.61	1.46	114.04	105.31
+H&OH	0.5	-368.9	1.58	1.47	113.09	105.72
	0	-341.3	1.59	1.47	113.60	105.59
	-0.5	-307.6	1.60	1.46	114.04	104.85

The adsorption energy of SO₃ is -241.7 kJ mol⁻¹ on the SO₂-adsorbed surface at zero field, which is lower than that on CO₂-adsorbed surface. Because SO₂ has higher ability to take charge than CO₂, charge transfer between SO₃ and the slab should be weaker on the SO₂-adsorbed surface, and the SO₃ adsorption energy should be smaller on SO₂ surface than that on CO₂-adsorbed surface. In the case when a small

electrostatic field is applied, the extent of reduction in adsorption energy of SO₃ is also larger than the case without SO₂, about 6.94 and 7.43 kJ mol⁻¹, as shown in Fig. 6 and Table 1. Then as the electrostatic field continues to increase, the adsorption energy required for the positive and negative electrostatic field gradually increases and decreases linearly, respectively.

Fig. 3. LDOS of SO_3 on $\text{CaO}(100)$ surface with electric field in or opposite the normal direction of the surface.

Effects of H_2O on SO_3 Adsorption in an Electrostatic Field

For H_2O adsorption on CaO surface, H_2O dissociates into surface OH and H atom, and H binds with O on CaO (Zhang et al., 2015; Jiang and Fang, 2016). Fig. 7 shows the adsorption energy of SO_3 on the surface of $\text{CaO}(100)$ under various electrostatic field conditions with H, OH and H&OH is adsorbed on the surface. In the case with H adsorbed on the surface, it can be clearly seen that the variation of adsorption energy is different with other cases. When the electrostatic

Fig. 4. The variation of charge transfer with respect to the electric field.

field is positive, the adsorption energy has a slight decrease first and then increases steadily. The total increment is much smaller than the previous cases, from $-295.8 \text{ kJ mol}^{-1}$ to $-305.1 \text{ kJ mol}^{-1}$. When the electrostatic field is negative, the adsorption energy would not decrease, but increase as the electrostatic field is higher than $0.05 \text{ V}/\text{\AA}$, and decrease slightly at $0.4 \text{ V}/\text{\AA}$. The total variation is negligible. Unlike the effect of CO_2 and SO_2 , pre-adsorbed H&OH is favorable for the binding of SO_3 on CaO surface, as shown in Table 1. The variation of adsorption energy with OH and H&OH adsorbed on the surface is similar to the other cases.

The charge transfer between the adsorbed SO_3 and CaO surface is characterized by CDD plots, which displays a large charge accumulation in the region between S and O_{CaO} and significant charge depletion in the region between the O_{CaO} in the top layer and the Ca ion in the second layer, as shown in Figs. 8 and S3. That confirms the formation of a strong bond between S and O_{CaO} . There is also an obvious charge accumulation around the O ion in the SO_4^{2-} -like structure, which is match up with the results of the charge transfer from the slab to the SO_4^{2-} -like structure, as shown in Fig. S4.

The positive field is seen to enhance charge density changes of the surface O across the Ca around the O_{CaO} , while the negative field enhances charge density changes of the Ca below the O_{CaO} . There is a small but essential difference in the CDD plots between the systems with adsorbed H and H&OH. When H is previously adsorbed, the SO_4^{2-} -like structure interacts more with Ca cations around it. However, when on a clean surface or H&OH is previously adsorbed, charge transfer is more between Ca and O on the surface.

CONCLUSIONS

The effects of electrostatic field on the interactions between SO_3 and a CaO surface were predicted from DFT calculations. Adsorption on a clean surface or surface with pre-adsorbed species, including CO_2 , SO_2 , OH, H&OH, is sensitive to the existence of an electrostatic field. When the field is small,

Fig. 5. Adsorption energies of (a) CO₂ on CaO(100) and SO₃ on CaO(100) surface with CO₂ adsorbed previously on (b) site ① and (c) site ② versus electric field.

Fig. 6. Adsorption energies of (a) SO_2 on $\text{CaO}(100)$ and (b) SO_3 on $\text{CaO}(100)$ surface with SO_2 adsorbed previously versus electric field.

the required adsorption energy is seen to reduce regardless of a positive or negative electrostatic field. Then, with increased field strength, the adsorption energy shows an increasing trend in a positive electrostatic field, while the adsorption energy decreases in a negative electrostatic field. A positive field enhances charge density changes of the surface O across the Ca around the O_{CaO} , while a negative field enhances charge density changes of the Ca below the O_{CaO} . On an H pre-adsorbed surface, the total increment is much smaller than previous cases in a positive field and the total variation is negligible in a negative field.

From the results of the charge transfer and CDD, it can be concluded that the SO_4^{2-} -like structure accumulates electrons as a unit. The charge transfer of SO_4^{2-} is found to increase with the incremental adsorption energy in a linear relationship.

There is obvious charge accumulation in the region between S and O_{CaO} and significant charge depletion in the region between the O_{CaO} in the top layer and the Ca ion in the second layer, which confirms the formation of a strong bond between S and O_{CaO} .

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Fig. 7. Adsorption energies of SO_3 on $\text{CaO}(100)$ surface with (a) H, (b) OH and (c) H and OH adsorbed previously versus electric field.

Fig. 8. CDD plot of SO_3 bound on the $\text{CaO}(100)$ surface with an electric field of $0.5 \text{ V/\AA}$; (a) and (b) clean CaO , (c) and (d) $-\text{H}$, (e) and (f) $-\text{H\&OH}$; (a), (c) and (e) is in a positive field; (b), (d) and (f) is in a negative field; charge accumulation is in yellow and charge depletion is in blue.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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