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# Pressure-dependent band-bending in ZnO: A near-ambient-pressure X-ray photoelectron spectroscopy study

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ZnO-based catalysts have been intensively studied because of their extraordinary performance in lower olefin synthesis, methanol synthesis and water–gas shift reactions. However, how ZnO catalyzes these reactions are still not well understood. Herein, we investigate the activations of  $CO_2$ ,  $O_2$  and CO on single crystalline ZnO polar surfaces at room temperature, through *in-situ* near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS). It is revealed that  $O_2$  and  $CO_2$  can undergo chemisorption on ZnO polar surfaces at elevated pressures. On the ZnO (0001) surface, molecular  $CO_2$  ( $O_2$ ) can chemically interact with the top layer Zn atoms, leading to the formation of  $CO_2^{-1}$  ( $O_2^{--}$ ) or partially dissociative atomic oxygen ( $O^-$ ) and hence the electron depletion layer in ZnO. Therefore, an apparent upward band-bending in ZnO (0001) is observed under the  $CO_2$  and  $O_2$  exposure. On the ZnO (0001) surface, the molecular chemisorbed  $CO_2$  ( $O_2$ ) mainly bond to the surface oxygen vacancies, which also results in an upward bandbending in ZnO (0001). In contrast, no band-bending is observed for both ZnO polar surfaces upon CO exposure. The electron-acceptor nature of the surface bounded molecules/atoms is responsible for the reversible binding energy shift of Zn  $2p_{3/2}$  and O 1s in ZnO. Our findings can shed light on the fundamental understandings of  $CO_2$  and  $O_2$  activation on ZnO surfaces, especially the role of ZnO in heterogeneous catalytic reactions.

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Abbreviations: NAP-XPS, near-ambient-pressure X-ray photoelectron spectroscopy; UHV, ultrahigh vacuum; NAP-STM, near-ambient-pressure scanning tunneling microscopy; CBM, conduction band minimum; ZnO, zinc oxide.

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### 1. Introduction

Zinc oxide (ZnO), a II-VI semiconductor with a wide band gap of 3.4 eV, has attracted tremendous attention because of its potential applications in optoelectronics, gas sensors, and catalysis [1–7]. Especially, ZnO-based catalysts have been widely used in the synthesis of methanol and light olefins [8–11]. Despite much theoretical and experimental efforts have been devoted to clarifying the mechanism of CO<sub>2</sub>, CO and H<sub>2</sub> activation on ZnO-based catalysts, it is still in debates about the actual active site on ZnO, for example, the ZnO-Cu interfacial site or the Zn-Cu bimetallic site [12–16]. For the synthesis of light olefins, Bao's group have successfully demonstrated that the activation of H<sub>2</sub> and CO occurred on partially reduced metal oxide surface [9].

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In order to further unravel the catalytic role of ZnO, it is essential to investigate the adsorption and activation processes of gas reactants on various ZnO surfaces. Low-temperature scanning tunneling microscopy studies revealed that CO<sub>2</sub> chemisorbed on ZnO

(1010) surface *via* a formation of a linear one-dimensional  $CO_2$  assembly along the [0001] directions of ZnO. The two oxygen atoms of  $CO_2$  bond to the neighbored Zn cations while the carbon atom sits on top of the substrate O ion. The formation of this chain structure was caused by the attractive dipole–dipole interactions between the chemisorbed  $CO_2$  molecules and the ZnO polar surface, which was supported by the density functional theory calculations [17]. For the  $O_2$  adsorption on ZnO, electron energy loss spectroscopy experiments confirmed that the oxygen chemisorbed in a state different from the molecular oxygen on Zn-polar ZnO sur-

face [18]. A partially reduced ZnO (1010) surface with oxygen vacancies was demonstrated to be energetically preferable for the dissociation of adsorbed molecular oxygen as compared to the stoichiometric ZnO ( $10\overline{10}$ ) surface using first-principles total-energy calculations [19].

However, most of these model studies were carried out in ultrahigh vacuum (UHV) conditions rather than a realistic reactive environment at elevated pressures. It is generally known that there is a pressure gap between the low pressure ( $<10^{-3}$  mbar) and that above millibar [20]. Some surface reactions that are not likely to occur under UHV conditions can be observed at near ambient pressures due to the entropic contribution to the system's Gibbs free energy [21-27]. Near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) can provide direct information on the chemical state of both catalysts and reaction intermediates during the catalytic processes under a wide range of pressures and temperatures [28]. For example, many pioneering works from M. Salmeron and G. Somorjai's groups have already demonstrated that NAP-XPS have a substantial impact in the heterogeneous catalysis and environmental chemistry studies [27,29-31]. Under near ambient pressure conditions, Porsgaard et al [32]. reported a reversible bandbending effect on the O<sub>2</sub> exposed TiO<sub>2</sub> samples. It is desirable to investigate the interaction between ZnO and gas reactants at the millibar pressure range for an in-depth understanding of the ZnO catalytic role in practical applications.

Herein, we investigated the interactions between ZnO and gas molecules ( $CO_2$ ,  $O_2$  and CO) at a wide pressure range using *insitu* NAP-XPS measurements. The exposure impacts of  $CO_2$  and  $O_2$  on the XPS core levels of ZnO polar surfaces have been demonstrated. It is revealed that  $CO_2$  and  $O_2$  may undergo molecular adsorption and dissociative adsorption on the ZnO polar surfaces. The adsorbed  $CO_2$  and  $O_2$  molecules and dissociative atomic oxygens may act as acceptors to deplete electrons in the ZnO polar surfaces. These reversible band-bending behaviors reveal possible weak chemisorption of  $CO_2$  and  $O_2$  on the ZnO polar surfaces, which may improve our fundamental understandings of ZnO based heterogeneous catalytic reactions.

### 2. Experimental

*In-situ* NAP-XPS experiments were performed in a laboratorybased SPECS Phoibos 150 NAP-XPS package equipped with a twin anode X-ray source (SPECS XR50, Al  $K\alpha$ , hv = 1486.6 eV; Mg  $K\alpha$ , hv = 1253.6 eV) and a UV source (Specs UVS 10/35, He I, hv = 21.2 eV) with a base pressure below  $5 \times 10^{-10}$  mbar. The preparation chamber is equipped with an ion sputter gun (Omicron ISE 10) and an e-beam sample heater (VG Scienta, EBHC) with a base pressure below  $6 \times 10^{-11}$  mbar. Two independent gas lines were used to introduce the gas into the NAP cell with the pressure range from UHV to several millibar within 2 minutes. The analysis chamber and gas lines were thoroughly baked before experiments. The sample was loaded near the 300  $\mu$ m nozzle of the NAP cell and illuminated by the X-ray through a 100 nm thick Si<sub>3</sub>N<sub>4</sub> window.

ZnO (0001) and ZnO (0001) single crystals ( $10 \times 10 \times 2$  mm) were cleaned in an ultrasonic bath before loading into the UHV chamber. The clean surfaces were obtained by 5 cycles of 1 keV Ar<sup>+</sup> sputtering for 15 minutes and subsequent annealing at 630 °C for 10 minutes. The samples were re-cleaned after each gas exposure. The cleanliness of the ZnO samples were checked by XPS measurements after the final cycle of pre-treatment.

The core-level spectra of Zn  $2p_{3/2}$  and O 1s were measured with an Al K $\alpha$  source. The pass energy was set at 20 eV and the binding energies of the XPS spectra were calibrated by the Au 4f of a sputter-cleaned Au (111) sample. The resolution of this instrument (Full width at half maximum, FWHM) was ~0.8 eV (Ag 3*d*). All NAP-XPS characterizations were conducted at room temperature once the chamber pressures reached the equilibrium conditions (~30 minutes). The core-level spectra were analyzed by CasaXPS with Shirley type backgrounds and GL (70) line shapes (a mixing of 30% Gaussian and 70% Lorentzian).

#### 3. Results and discussion

The ultraviolet photoelectron spectroscopy (UPS) of clean ZnO (0001) and ZnO (0001) samples were taken in the UHV conditions before they were loaded separately into the NAP-cell at room temperature (Fig. S1). Both surfaces have similar O 2*p* dominated valence band structures with band gap states extended to 1 eV below the Fermi level [33,34]. The gas was introduced into the NAP-cell from UHV to 0.5 mbar gradually and the XPS spectra collection was performed after 30 minutes for each pressure.

Fig. 1(a and b) show the evolution of Zn  $2p_{3/2}$  peaks of Znterminated ZnO (0001) and O-terminated ZnO (0001) surfaces at elevated CO<sub>2</sub> pressures. A progressive shift of the Zn  $2p_{3/2}$  peak to the lower binding energy region was observed with increasing CO<sub>2</sub> pressures. An overall lower binding energy shift of ~0.5 eV was found when the ZnO (0001) surface was exposed to 0.5 mbar CO<sub>2</sub>. The evolution of corresponding O 1s peak after CO<sub>2</sub> exposure was presented in Fig. 1(c and d).

It should be noted that the degree of peak shifts of Zn  $2p_{3/2}$  and O 1s were almost the same and the peak-shapes remained nearly unchanged during the gas exposure for both ZnO (0001) and ZnO

(0001) polar surfaces. This can rule out the possibility of new chemical states formation, which might lead to the significant changes in the peak shape [35]. Such peak shifts therefore can be explained by the band-bending effect occurred on the ZnO polar surfaces. Generally, the changes in charge carrier concentration and distribution will lead to the appearance of the band-bending, which can be effectively modulated by charge segregations and molecule/atom adsorptions. Segregation is a diffusional process that the charge is derived from the lattice, which could induce the formation of charge concentration gradients and hence the band-bending effect [36]. Adsorption sometimes can also cause the charge transfer between the substrate surface and adsorbates, resulting in a band-bending effect at the interfaces. Generally, the Segregation induced band-bending may only take place at high temperatures when the lattice elements are sufficient mobile [37]. Thus, we suggest that the observed pressure-dependent binding energy shifts at room temperature are mainly caused by the adsorption of CO<sub>2</sub> on the ZnO surfaces. Esken et al. have studied that  $CO_2$  can chemisorb on the top-lay Zn atoms of ZnO (0001) or

oxygen vacancies of ZnO (000 1) even at 100 K [38]. However, there are still debates on the nature of these chemisorptions, such as the formation of singly ionized molecular species of  $CO_2^-$  via non-



**Fig. 1.** XPS spectra of (a, b) Zn  $2p_{3/2}$  and (c, d) O 1s on ZnO (0001) (panels a and c) and ZnO (0001) (panels b and d) surfaces under varied pressure of CO<sub>2</sub>; (e) the evolution of pressure-dependent Zn  $2p_{3/2}$  and O 1s peak shifts under CO<sub>2</sub>; (f) the relative peak shifts of Zn  $2p_{3/2}$  and O 1s of ZnO (0001) under repeated UHV/CO<sub>2</sub> exposure measurements.

dissociative adsorption or singly ionized oxygen ions of O<sup>-</sup> via dissociative adsorption [39–41]. It has been reported that carbonates are formed on the surface for molecular adsorption of CO<sub>2</sub> on both ZnO polar surface [42–44]. But Dutta et al. [45] argued that the adsorption of CO<sub>2</sub> on the oxygen vacancy sites of ZnO (0001) surface has a bent structure of  $CO_2^-$ , which exposes the carbon atom for further reactions. Surface adsorbed  $CO_2^{\sigma-}{}_{(ad)}$  is also observed on the ZnO/Cu model catalyst during the CO<sub>2</sub> hydrogenation reactions using NAP-XPS measurements [46]. In our room temperature experiments, we did not observe any noticeable formation of the carbonates and surface adsorbed  $\text{CO}_{2^{-}(\text{ad})}^{\sigma-}$ , where the C 1s (O 1s) should locate around 289 eV and 288.5 eV (531 eV), respectively. (see Figs. S2(c and d)). Therefore, we suggest that the strong chemisorption may not be a dominant effect here for the surface band-bending behaviors or the coverage of carbonate/ $CO_{2}^{\sigma-}(ad)$  is too low to be captured. It was reported that the charged chemisorbed species can saturate on the surface with no more than 10<sup>-3</sup> monolayer because of the Weisz limitation, which is definitely below the detection limit of our XPS [47].

Fig. 1(f) shows the evolution of Zn  $2p_{3/2}$  and O 1s peak shifts of the ZnO (0001) surface under the repeated cycles of CO<sub>2</sub> exposure from  $5 \times 10^{-10}$  mbar to 0.5 mbar. It clearly reveals a highly reversible upward band-bending of the ZnO (0001) surface induced by the CO<sub>2</sub> exposure. The binding energies of Zn  $2p_{3/2}$  and O 1s moved back to their original values when the UHV environment was recovered. In contrast, the core levels in ZnO (0001) cannot shift back completely to their original positions upon the cyclical expo-

sure to  $CO_2$  (Fig. S4(a and b)). The different response of ZnO polar surfaces toward  $CO_2$  may be caused by the different surface chem-

ical environments, where the oxygen vacancies on ZnO (0001) are more active in comparison with the top-layer Zn of ZnO (0001) [38]. As aforementioned, we propose that the observed reversible band-bending is caused by the weak chemisorption of CO<sub>2</sub> on the ZnO surface and the associated interfacial charge transfer. Similar reversible band-bending effect has been studied by photoluminescence (PL), NAP-XPS and theoretical calculation. Stevanovic et al. [48] reported that the adsorption of NH<sub>3</sub> and CO on TiO<sub>2</sub> can lead to a downward band-bending, which is reversible upon the desorption of NH<sub>3</sub>/CO. The authors also mentioned an irreversible bandbending effect upon O<sub>2</sub> exposure and ascribed it to the dissociation of O<sub>2</sub> on the TiO<sub>2</sub> surface. However, Porsgaard et al. [32] studied the interaction of  $O_2$  with TiO<sub>2</sub> (110) using NAP-XPS and found that the O<sub>2</sub> adsorption induced surface band-bending on TiO<sub>2</sub> (110) surface is reversible. Generally, the dissociative adsorption of oxygen was ruled out since the recombination of oxygen atoms on TiO<sub>2</sub> (110) surface is difficult. From our previous study [49], we observed the band-bending effect of ZnO polar surfaces upon H<sub>2</sub> exposure, which is reversible on ZnO (0001) and irreversible on (0001). Combined with theoretical calculation, we found that the H<sub>2</sub> was activated by both ZnO polar surfaces and dissociatively adsorbed on the top-layer Zn of ZnO (0001) and top-lay O of ZnO (0001). The adsorption energy of H on ZnO (0001) was small and could easily recombine and desorb from surface, thus resulting in

reversible band-bending behavior. In contrast, the adsorption



Fig. 2. XPS spectra of (a, c) Zn 2p<sub>3/2</sub> and (b, d) O 1s on ZnO (0001) (panels a and b) and ZnO (0001) (panels c and d) surfaces under varied pressure of CO.

energy of H on ZnO (0001) was 2.43 eV, the formation of stable surface hydroxyl leads to an irreversible band-bending on ZnO (0001) surface.

In the current study, the CO<sub>2</sub> gas molecules are estimated to weakly bind on the top-layer Zn of ZnO (0001) to form  $CO_2^{\delta-}$ instead of carbonate since the carbonate is not likely to desorb from the substrate surface at room temperature [44]. In contrast, the adsorption of CO<sub>2</sub> on ZnO (000 1) may result in the formation of carbonate on the oxygen vacancy and thus an irreversible band-bending (Fig. S4) [43,50]. When we consider the dissociative chemisorption of CO<sub>2</sub> on the ZnO (0001) surface, the dissociated atomic O species may react with Zn to form an O<sup>-</sup> (electron acceptor) [51–53]. The formation of O<sup>-</sup> led to electron depletion in ZnO (0001) and hence the Fermi level of ZnO (0001) moved away from the conduction band minimum (CBM). As a result, an upward band-bending was observed under  $CO_2$  exposure.

It is worth noting that the overall binding energy shifts of Zn  $2p_{3/2}$  and O 1s were larger on ZnO (0001) than that on ZnO (0001) as shown in Fig. 1(e), which can be attributed to three reasons: firstly, ZnO (0001) polar surface shows an excess of electrons as compared with the ZnO (0001) polar surface [55–56]. Secondly, the different electronic nature of (0001) and (0001) polar surfaces (Fig. S(1)). The valence band is located at ~3.15 eV and ~2.85 eV below the Fermi level for ZnO (0001) and ZnO (0001), respectively[57], suggesting that electrons could be transferred to the gas adsorbates (electron acceptor) more energetically favorable

on ZnO (0001) surface as compared to ZnO (0001). Thirdly, the adsorption tendencies of the atomic oxygen on ZnO (0001) and ZnO (0001) is different. Previous studies have suggested that the adsorption enthalpies of atomic oxygen on ZnO (0001) is slightly more favorable than that on ZnO (0001) surface ( $\Delta H_{ads} = 0.4 \text{ eV}$  per O adatom) [54]. Therefore, more oxygen species could adsorb on the ZnO (0001) surface and accept more electrons from the oxides.

As discussed above, the dissociative adsorption of CO<sub>2</sub> on ZnO surfaces might come with an active atomic O and a CO\* fragment. However, the effect of CO adsorption on the surface band-bending is unknown. Thus, in situ NAP-XPS measurements were also carried out to investigate the electronic structures of ZnO polar surfaces upon CO exposure. As shown in Fig. 2, we did not observe any apparent binding energy shifts, nor the appearance of new shoulders in Zn  $2p_{3/2}$  and O 1s on both ZnO (0001) and ZnO (0001) surfaces upon exposing to 0.5 mbar CO, suggesting a relatively weak electronic interaction between CO molecule and the ZnO polar surfaces. This observation is consistent with previous reports that the molecular CO only physisorbed on oxides surface at low temperatures [58-60]. Therefore, in the consideration of CO<sub>2</sub> adsorption/ desorption induced reversible band-bending on ZnO, the molecular chemisorption of CO<sub>2</sub> might play the major role although the dissociated chemisorption of CO<sub>2</sub> cannot be completely ruled out. One possibility is that a small part of CO<sub>2</sub> dissociate on the ZnO (0001) and leave the atomic oxygen on the surfaces, and the reversible band-bending is caused by the adsorption (desorption) of these O species in the presence of  $CO_2$  (after the evacuation of  $CO_2$ ).

It was reported that ZnO (0001) surface is less active than other ZnO surfaces for some electronegative adsorbates, such as CO<sub>2</sub> and O<sub>2</sub> [61]. However, our aforementioned results show that the ZnO (0001) surface has stronger interaction for CO<sub>2</sub> adsorptions than that on the ZnO (0001) surface. To further verify the activity of ZnO polar surfaces, we study the electronic interactions between O<sub>2</sub> and ZnO. Fig. 3 show the pressure-dependent evolution of Zn 2p<sub>3/2</sub> and O1s on ZnO (0001) and ZnO (0001) upon the O<sub>2</sub> exposure. Both Zn 2p<sub>3/2</sub> and O1s shifted to the lower binding energy region after the O<sub>2</sub> exposure, and an overall shifts of ~0.6 eV and ~0.3 eV were observed on ZnO (0001) and ZnO (0001) surfaces respectively under the O<sub>2</sub> pressure of 0.5 mbar. This upward band-bending under the O<sub>2</sub> exposure was reversible on the ZnO (0001) surface and non-fully reversible on ZnO (0001) (Fig. 3(f) and Fig. S4(f)).

Similar to CO<sub>2</sub> exposure, the pressure-dependent reversible band-bending effect may be caused by the molecular chemisorption or dissociative chemisorption of O<sub>2</sub> on polar ZnO surfaces. For the molecular chemisorption, the charge transfer takes place between the adsorbed O<sub>2</sub> molecules and the ZnO polar surfaces. The relatively weak interaction between the molecular O<sub>2</sub> and ZnO (0001) is responsible for the reversible band-bending during the O<sub>2</sub> exposure and evacuation cycles [62]. The oxygen vacancies on ZnO (0001) will trap the molecular O<sub>2</sub> and result in an irreversible band-bending [63]. For the dissociative adsorption, it has been reported that the O<sub>2</sub> will dissociate on the ZnO polar surfaces to form oxygen atoms at near ambient pressure [64,54], where the



**Fig. 3.** XPS spectra of (a, b) Zn  $2p_{3/2}$  and (c, d) O 1s on ZnO (0001) (panels a and c) and ZnO (0001) (panels b and d) surfaces under varied pressure of O<sub>2</sub>; (e) the evolution of pressure-dependent Zn  $2p_{3/2}$  and O 1s peak shifts under O<sub>2</sub>; (f) the relative peak shifts of Zn  $2p_{3/2}$  and O 1s of ZnO (0001) under repeated UHV/O<sub>2</sub> exposure measurements.



**Fig. 4.** Proposed model for  $CO_2$  and  $O_2$  adsorbed on ZnO polar surfaces, where the grey, red, black and transparent red spheres represent Zn, O, C atoms and O vacancy, respectively; (a) the model for  $CO_2/O_2$  on ZnO (0001): non-dissociated  $CO_2/O_2$  adsorption and dissociated  $CO_2/O_2$  adsorption, the transparent bond between the adsorbate and surface Zn atom represents a relatively weak interaction that only exists in the presence of gas molecules; (b) the model for  $CO_2/O_2$  on ZnO (0001): molecular  $CO_2/O_2$  adsorption and strong  $CO_2/O_2$  chemisorption, the molecules in the dash boxes represent the irreversible chemisorption on the O vacancies; (c) the band structure of ZnO surfaces upon the interaction with  $CO_2/O_2$  gas molecules.

atomic oxygen bonds to the top-layer Zn atom to the form  $O^-$  (acceptor) on the ZnO (0001) surface.

Based on our NAP-XPS results and discussions, we propose two possible adsorption pathways for CO<sub>2</sub> and O<sub>2</sub> molecules on ZnO polar surfaces: molecular chemisorption and dissociated chemisorption. For molecular chemisorption (Fig. 4(a)), the CO<sub>2</sub>/ O<sub>2</sub> molecules will accept electrons from the ZnO (0001) surface to form  $CO_2^{\delta-}/O_2^{\delta-}$  once they adsorb on the substrate [65]. For dissociative chemisorption (Fig. 4(a)), partial CO<sub>2</sub>/O<sub>2</sub> molecules might be activated and dissociated by the ZnO (0001) surface to form O<sup>-</sup> on top-layer Zn atoms to accept electrons from the ZnO surface. It should be noted that both kinds of the adsorption on the ZnO (0001) is relatively weak, and these adsorbates can easily desorb from the surface upon the evacuation of the gas cell. The adsorp-

tion of  $CO_2/O_2$  on the ZnO (0001) is proposed to be molecular chemisorption as shown in Fig. 4(b). The dash boxes indicate the strong chemisorption of  $CO_2/O_2$  on the oxygen vacancy which represents the irreversible band-bending upon the pumping of gas. Fig. 4(c) schematically illustrates the band structure that is affected by the adsorbates under the gaseous environments. As the electron depletion layer formed between the ZnO polar surfaces and  $CO_2^{3-}/O_2^{5-}/O^{-}$ , the surface band will bend upward.

#### 4. Conclusions

Using *in-situ* NAP-XPS measurements, we investigated the pressure-dependent band-bending effects on ZnO polar surfaces. Two possible mechanisms were proposed and discussed. For the molecular chemisorption, the  $CO_2$  ( $O_2$ ) most likely interact with the top-layer Zn atom of ZnO (0001) and oxygen vacancy of ZnO (0001) with associated electron transfer from the ZnO polar surfaces to the adsorbates, which resulting in an upward bandbending. For the dissociative chemisorption, the  $CO_2$  ( $O_2$ ) might

dissociate on ZnO (0001) surface to form atomic oxygen and these dissociated atomic oxygen can react with the top-layer Zn atoms of ZnO (0001), leading to an electron depletion in ZnO and hence an upward band-bending. In contrast, the CO exposure did not induce

any obvious band-bending on both ZnO (0001) and ZnO (0001) surfaces. Our findings reveal that  $CO_2$  and  $O_2$  can be activated on polar ZnO surfaces at room temperature, which can help to provide a better understanding of ZnO catalytic roles in methanol synthesis and light olefin conversion.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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