1	Novel kinetic modeling of photocatalytic degradation of ethanol and acetaldehyde in air by
2	commercial and reduced ZnO: effect of oxygen vacancies and humidity
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14	Abstract
15	A comprehensive kinetic model was developed to address the factors and processes governing the
16	photocatalytic removal of gaseous ethanol by using ZnO loaded in a prototype air purifier. This model
17	simultaneously tracks the concentrations of ethanol and acetaldehyde (as its primary oxidation product) in
18	both gas phase and on the catalyst surface. It accounts for reversible adsorption of both compounds to
19	assign kinetic reaction parameters for different degradation pathways. The effects of oxygen vacancies on
20	the catalyst were validated through the comparative assessment on the catalytic performance of
21	commercial ZnO before and after the reduction pre-treatment (10% H ₂ /Ar gas at 500°C). The influence
22	of humidity was also assessed by partitioning the concentrations of water molecules across the gas phase
23	and catalyst surface interface. Given the significant impact of adsorption on photocatalytic processes, the

24 beginning phases of all experiments (15 min in the dark) were integrated into the model. Results showed 25 a notable decrease in the adsorption removal of ethanol and acetaldehyde with an increase in relative humidity from 5% to 75%. The estimated number of active sites, as determined by the model, increased 26 from 7.34 10⁻⁶ in commercial ZnO to 8.86 10⁻⁶ mol g_{cat}⁻¹ in reduced ZnO. Furthermore, the model predicts 27 28 that the reaction occurs predominantly on the catalyst surface while only 14% in the gas phase. By using 29 quantum yield calculations, the optimal humidity level for photocatalytic degradation was identified as 25%, showing highest quantum yield of 6.98 10⁻³ (commercial ZnO) and 10.41 10⁻³ molecules photon⁻¹ 30 31 (reduced ZnO) catalysts.

32 Keywords

33 Kinetic modelling, air treatment, ethanol degradation, oxygen vacancy, ZnO photocatalyst

35 1. Introduction

36 Indoor air quality is a crucial health concern [1, 2], particularly as urban residents spend roughly 90% 37 of their time indoors, including residential and public areas [3]. Next to particulate matter, volatile organic 38 compounds (VOCs) are the leading causes of indoor air pollution [4, 5]. Compounds such as ethanol and 39 acetaldehyde are emitted indoors from various sources such as cleaning products, food, building materials, 40 and personal care products [6, 7], and can lead to various health problems, including respiratory irritation, 41 headaches, and dizziness, especially when inhaled at high concentrations [8, 9]. The U.S. Occupational 42 Safety and Health Administration (OSHA) gives a threshold limit value for acetaldehyde of 25 ppm [10]. 43 Moreover, long-term exposure to ethanol has been associated with liver and kidney damage and an 44 increased risk of cancer [11]. Therefore, it is important to efficiently mitigate these harmful compounds 45 from indoor air to ensure a healthy living environment.

46 Over the past few decades, the popularity of photocatalysis has increased significantly as an eco-47 friendly environmental remediation technology [12, 13]. Zinc oxide (ZnO) is widely used as a 48 photocatalyst due to its beneficial properties such as high removal efficiency, low cost, non-toxicity, and 49 unique optical and electronic features [14, 15]. However, its application has a number of limitations such 50 as a relatively high bandgap (3.2-3.4 eV), photocorrosion, and a high recombination rate of electron-hole 51 pairs [16, 17]. Recent studies suggest that the modification or formation of surface oxygen defects can be 52 an effective approach to enhance the photocatalytic activity of semiconductor catalysts [18, 19]. Such 53 defects can act as charge traps and adsorption sites, facilitating the effective transfer of photo-induced 54 electrons to the adsorbates. This can suppress electron-hole recombination while also degrading adsorbate 55 molecules via charge transfer [20].

57 One key environmental issue with application of photocatalytic processes, is potential generation of 58 intermediates that are more hazardous than the original pollutant [21, 22]. A good example is acetaldehyde, 59 produced as the main byproduct of ethanol oxidation [22]. The concentrations of ethanol and acetaldehyde 60 in indoor air of a French hospital were found at 245.7 and 10.5 μ g m⁻³, respectively [23]. According to the 61 National Fire Protection Association (NFPA), ethanol has a health hazard index of 2, while acetaldehyde 62 has a higher index of 3, indicating greater exposure risk. Therefore, the incomplete photocatalytic 63 degradation of ethanol can pose a higher exposure risk through the formation of acetaldehyde.

To gain a better knowledge on the mitigation of VOCs, efforts were made to address the role of the key 64 65 factors (such as oxygen vacancies and humidity) in regulating the photocatalytic degradation of ethanol and its byproduct, acetaldehyde. For the first time, a kinetic model was developed to consider not only the 66 67 adsorption and photocatalytic degradation of ethanol but also the simultaneous production and degradation 68 of acetaldehyde. By using selected ion flow tube mass spectrometry (SIFT-MS) equipment, the 69 concentrations of ethanol and acetaldehyde were continuously monitored and the model parameters were 70 estimated through curve fitting with the experimental data. To enhance catalytic efficiency, oxygen 71 vacancy enriched ZnO was created through hydrogen reduction pretreatment. Additionally, the effect of 72 relative humidity was incorporated into the kinetic model to describe the adsorption and photocatalytic 73 degradation behavior in relation to humidity levels.

74 2. Materials and methods

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2.1 Materials and catalyst preparation

Ethanol (CAS: 64-17-5), acetaldehyde (CAS: 75-07-0), and commercial ZnO (named as C-ZnO) with product number of 544906, used as photocatalyst, were obtained from Sigma-Aldrich. The oxygen vacancies in the catalyst were generated by following the same procedures reported in our previous study 79 [24]. To briefly summarize, hydrogen reduction of the commercial catalyst was performed using an 80 AutoChem II system (Norcross, USA). A pretreatment procedure was employed in order to cleanse the 81 catalyst surface of adsorbed molecules, such as water, oxygen, or CO₂. The C-ZnO was heated to 130 °C 82 under a stream of He (flow rate 60 cm³/min) and then cooled to room temperature. Thereafter, the gas flow 83 was changed to 10% H₂/Ar at a flow rate of 60 cm³/min, and the temperature was ramped up to 500 °C at 84 a rate of 10 °C/min. The sample was held at 500 °C for 5 hours to ensure effective reduction of the catalyst. 85 This reduced catalyst is named R-ZnO in this study.

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2.2 Reactor setup and photocatalytic experimental procedure

87 The reactor setup is illustrated in Figure 1. A commercially available photocatalytic mini air purifier 88 (model LHS002KEK) provided by LocknLock company, Seoul, South Korea, was modified for the 89 intended experimental conditions [25, 26]. The original ceramic and dust filters of the air purifier were 90 removed and replaced by in-house coated catalyst materials. Plain ceramic filters made of a mixture of 91 silicon carbide and aluminum oxide were purchased from Shengquan group, Jinan, China (10PPI) and used 92 as a bed for catalyst coating. ZnO nanoparticles were coated onto the ceramic filters using the drop-cast 93 method [27-29]. The required amount of ZnO was added to 10 mL ethanol and sonicated for 30 minutes. 94 The suspension of nanoparticles was then distributed uniformly onto the ceramic filter by drops of less than 5 µL using a micropipette. During the coating process, the ceramic filter was placed on a hot plate at 95 96 70 °C to increase the evaporation rate of ethanol. Subsequently, the coated ceramic was heated at 100 °C 97 for 12 hours to ensure that all ethanol had evaporated. The mass of the ceramic filter was measured before 98 and after the coating process to ensure that it was effectively coated. More than 95% of the catalyst 99 remained on the ceramic filter after coating. Pictures of the ceramic filters taken before and after ZnO 100 coating as shown in Figure S.1 in the Supplementary Information.

The spectrum of the light source of the commercial air purifier was measured by an AvaSpec-ULS2048CL-EVO optic spectrometer, produced by Avantes, Netherland. Figure S.2 shows the light spectrum data, with the majority of the emitted light in the UVA range with a peak at 368 nm. The air purifier was modified to control the light conditions of the process by installing a light/dark switch. This allows the study of ethanol adsorption on the surface of the catalyst under dark conditions.

106 The reactor chamber was constructed from polypropylene and had a volume of 16 L with dimensions 107 of 32 x 24 x 21 cm. The air pump of the air purifier provided three different flow rate settings: 100, 130, 108 and 160 L/min. To ensure thorough mixing of the air inside the reactor chamber, an additional fan (Gegei 109 mini fan, Shenzhen, China.) was also employed. Prior to each experiment, the chamber was purged with dry air (21% O₂ and 79% N₂) to remove any residual compounds. The required volumes of liquid ethanol 110 111 and water to reach the intended concentration and humidity for each experiment were then injected into 112 the chamber by Hamilton gastight micro-syringe (Reno, USA) and allowed to completely evaporate and 113 homogeneously mix for 15 minutes. The humidity of the air within the chamber was monitored with a 114 Dostmann LOG220-E sensor (Wertheim, Germany) and the production of CO2 was measured on certain 115 moments using Vaisala GMP222 (Vantaa, Finland) CO2 sensor.

116 All experiments were conducted at a room temperature of 25 ± 2 °C. The concentrations of ethanol, 117 acetaldehyde, and formaldehyde in the reactor chamber were continuously monitored using a Voice 200® 118 (SYFT Technologies Ltd., Interscience, Louvain-la-Neuve, Belgium) selected-ion flow-tube mass 119 spectrometer (SIFT-MS). Prior to entering the SIFT-MS equipment, the gas from the reactor was 120 continuously sampled at a flow of 5 mL/min and diluted by a flow of 25 mL/min of N2 gas. The SIFT-MS 121 equipment generates precursor ions of H₃O⁺, NO⁺, and O₂⁺ in a discharge ion source, selects a specific 122 precursor using a quadrupole mass filter, and then injects the selected precursors into a fast-flowing He 123 carrier gas in a flow tube. Gas molecules in the sample react with the precursor ions, and the resulting product ions are measured every 20 seconds (depending on the number of product ions selected for measurement) by a downstream quadrupole mass spectrometer in the m/z range of 15 to 250 [30-32]. The details about the reactions between precursor ions and the analytes (ethanol and acetaldehyde) and the subsequent calculations of the analyte concentrations are provided in section S.3 of the Supplementary Information.

To verify that the adsorption and photocatalytic degradation of ethanol were solely due to the ZnO catalyst, a control experiment was also conducted using an uncoated ceramic filter and UV lights. The results of the control experiment are presented in Figure S.3. As shown, there was no reduction in ethanol concentration due to either photolysis (without catalyst) or adsorption on the uncoated ceramic filter.

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2.3 Catalyst characterization methods

134 The Micromeritics AutoChem II equipment was used to perform temperature-programmed reduction 135 (TPR) and pulse chemisorption oxidation (PCO) of the ZnO catalysts. For TPR analysis, a pretreatment of 136 200 mg of C-ZnO was performed with He (flow rate of 60 cm³/min at 130 °C). The sample was then cooled 137 to room temperature and the flow was switched to 10% H₂/Ar. The temperature was gradually raised to 138 650 °C at a ramping rate of 10 °C/min. Water molecules produced from the hydrogen reduction of ZnO 139 were separated from the gas stream by means of a cold trap, set at -80 °C. For PCO analysis, 200 mg of C-140 ZnO or R-ZnO catalyst was heated to 500 °C under an Ar stream (flow rate of 30 cm³/min) as the carrier 141 gas. Pulses of 5% O₂/Ar, with a loop volume of 0.486 cm³, were injected into the carrier gas, and the 142 consumption of oxygen due to re-oxidation of ZnO was monitored using a thermal conductivity detector. 143 A JEOL-7610F PLUS electron microscope (Tokyo, Japan) was used to conduct both field emission 144 scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses. The 145 elemental composition of the catalysts was determined through EDS mapping, which allowed the detection

146 of 1 million points in an area of approximately 1 square micrometer. A Thermo ScientificTM K-AlphaTM

147 XPS system (Waltham, USA) was utilized to conduct XPS analysis. EPR spectra were generated using a 148 Bruker EMX plus equipment (Billerica, USA) at room temperature, with a 100 kHz field modulation 149 frequency and a microwave frequency of 9.64 GHz on the X-band spectrometer. Powder XRD analysis 150 was performed using a Rigaku Ultima IV (Tokyo, Japan), with a Cu ($\lambda = 1.54059$ Å) radiation source of 151 40 kV and 40 mA, and a scanning speed of 0.02 deg/sec. Quantachrome Autosorb-iQ 2ST/MP equipment 152 (Boynton Beach, USA) was used to perform adsorption-desorption isotherms analysis, with ultrapure 153 nitrogen gas at 77.35 K. All samples were degassed for 2 hours under vacuum at 150°C. The surface area 154 of the samples was measured by the Brunauer-Emmett-Teller (BET) method, while the pore volumes were 155 calculated by the nonlocal density functional theory (NLDFT) [33, 34]. The bandgap value of each catalyst 156 was found by Tauc plot [35, 36]. The solid nanoparticles were subjected to diffuse reflectance spectroscopy 157 (DRS) using PerkinElmer® Lambda 1050 spectrophotometer. The photoluminescence of the catalysts was 158 then analyzed using a LabRAM Aramis apparatus (Horriba Jovin Yvon company, Kyoto, Japan) by 159 plotting spectra for each catalyst using a He-Cd 325 nm laser, within a wavelength range of 325 to 900 160 nm.

161 **2.4 Kinetic model**

162 The kinetic model in this study is based on our previously developed model [37], which was specifically 163 designed for adsorption and photocatalytic degradation of micro-pollutants in water in relation to pH 164 changes. In contrast, the new model presented here is tailored for gas-phase reactions to consider the 165 influence of air humidity. The model accounts for the reversible adsorption and desorption processes 166 followed by the photocatalytic degradation of ethanol and its primary product, acetaldehyde, in both gas 167 phase and on the catalyst surface. As there was no noticeable increase in the concentration of formaldehyde 168 within the chamber, the possibility for the generation of formaldehyde through the degradation of ethanol 169 was excluded in the equations for the sake of simplification.

Eqs (1) to (7) depict the kinetic model employed in this study. Eq (1) tracks the variation in the concentration of ethanol in the air ($C_{g,E}$), which is influenced by the adsorption and desorption coefficients, $k_{1,E}$ (g mol⁻¹ min⁻¹) and $k_{2,E}$ (g L⁻¹ min⁻¹), respectively. C* represents the concentration of free active sites. The second part of Eq (1) denotes the photocatalytic degradation of ethanol in the gas phase by superoxide and hydroxyl radicals, represented by $k_{3,E}$ (min⁻¹) and by and $k_{4,E}$ (L mol⁻¹ min⁻¹), respectively. The concentration of adsorbed ethanol is defined as $C_{ad,E}$, while $C_{g,E}$ corresponds to the concentration of ethanol in the air. The volume of the reactor is V.

Eq (2) describes the concentration of ethanol at the surface of the catalyst, taking into account the degradation by electron-holes and hydroxyl radicals, with degradation coefficients of $k_{5,E}$ (min⁻¹) and $k_{6,E}$ (g mol⁻¹ min⁻¹), respectively. The adsorbed concentration of water molecules at the surface of the catalyst is denoted as $C_{ad,w}$, along with m_{cat} as the catalyst mass.

181 Eqs (3) and (4) describe the concentration of acetaldehyde in the air (Cg,A) and on the catalyst surface 182 ($C_{ad,A}$), respectively. The parameters $k_{1,A}$ to $k_{6,A}$ correspond to the same definitions as parameters $k_{1,E}$ to k_{6.E}, respectively, but for acetaldehyde instead of ethanol. However, to account for the production of 183 acetaldehyde from ethanol, a third term is added to the equations. Specifically, k_{3,EA} (min⁻¹) and k_{4,EA} (L 184 mol⁻¹ min⁻¹) represent the production of acetaldehyde from the oxidation of ethanol in the air by superoxide 185 and hydroxyl radicals, respectively. Meanwhile, k_{5,EA} (min⁻¹) and k_{6,EA} (g mol⁻¹ min⁻¹) represent the 186 187 production of acetaldehyde from the oxidation of ethanol on the catalyst surface by electron-holes and 188 hydroxyl radicals, respectively.

$$V \frac{dC_{g,E}}{dt} = -V(k_{1,E}C_{g,E}C_* - k_{2,E}C_{ad,E}) - V(k_{3,E}C_{g,E} + k_{4,E}C_{g,E}C_{g,w})\xi$$
(1)
$$m_{cat} \frac{dC_{ad,E}}{dt} = +V(k_{1,E}C_{g,E}C_* - k_{2,E}C_{ad,E}) - m_{cat}(k_{5,E}C_{ad,E} + k_{6,E}C_{ad,E}C_{ad,w})\xi$$
(2)

$$V \frac{dC_{g,A}}{dt} = -V(k_{1,A}C_{g,A}C_* - k_{2,A}C_{ad,A}) - V(k_{3,A}C_{g,A} + k_{4,A}C_{g,A}C_{g,w})\xi$$

$$+V(k_{3,EA}C_{g,E} + k_{4,EA}C_{g,E}C_{g,w})\xi$$
(3)

$$m_{cat} \frac{dC_{ad,A}}{dt} = +V(k_{1,A}C_{g,A}C_* - k_{2,A}C_{ad,A}) - m_{cat}(k_{5,A}C_{ad,A} + k_{6,A}C_{ad,A}C_{ad,W})\xi$$

$$+m_{cat}(k_{5,EA}C_{ad,E} + k_{6,EA}C_{ad,E}C_{ad,W})\xi$$
(4)

$$C_{ad,w} = k_w P_w C_* \tag{5}$$

$$C_* + \frac{(C_{ad,E} + C_{ad,A})}{a} + \frac{C_{ad,w}}{b_i} = C_{tot}$$
(6)

$$\begin{cases} \xi = 0 & , \quad t < t^* \\ \xi = 1 & , \quad t^* \le t \end{cases}$$
(7)

Eq (5) expresses the concentration of adsorbed water $C_{ad,w}$ (mol g⁻¹) on the catalyst surface, which is 190 dependent on the water adsorption coefficient k_w (kPa⁻¹), water vapor pressure P_w (kPa), and the 191 192 concentration of free active sites C* (mol g^{-1}). Eq (6) describes the active site balance, where the total concentration of active sites C_{tot} (mol g^{-1}) is equal to the sum of the free active sites and those occupied by 193 water, ethanol, and acetaldehyde. Since multi-layer adsorption of water and ethanol has been reported [38, 194 195 39], parameters a and b are used to represent the number of layers of adsorbed ethanol/acetaldehyde and 196 water, respectively. Moreover, since increasing humidity leads to an increase in the number of adsorbed 197 water layers [40, 41], the index i in parameter b is used to represent each humidity level (5%, 25%, 50%, 198 and 75%) tested in this work.

Eq (7) for the light/dark switch conditions is used to assess the effect of light on the photocatalytic degradation of ethanol and acetaldehyde. In the first 15 minutes of the experiments, photocatalytic degradation is not considered under the light off conditions (ξ =0). Hence, the removal of the compounds is only due to adsorption in the dark. After 15 minutes from the start of the experiments, the lights are switched on (ξ =1) to initiate the photocatalytic degradation. The photocatalytic degradation terms are then included in the model, as described in Eqs (1) to (4).

In-house code using Excel[®] software was utilized to perform the numerical integration of Eqs (1) to (4) for each 30-seconds time step. For the experiments 8 to 17 of Table 1, the initial conditions for the start of the numerical integration (t=0) were $C_{g,E} = C_0$, $C_{g,A} = 0$, $C_{ad,E} = 0$, and $C_{ad,A} = 0$. With the same approach, the initial conditions for experiments 18 to 25 were considered as $C_{g,E} = 0$, $C_{g,A} = C_0$, $C_{ad,E} = 0$, and $C_{ad,A} = 0$. Kinetic parameters were estimated by minimizing the residual sum of squares (RSSQ), as expressed by Eq (8), using a GRG nonlinear solving method. The total number of experimental data points for each experiment was denoted by N_i , while n represented the total number of experiments in the modeling.

$$S = \sum_{i=1}^{n} \sum_{j=1}^{N_j} (C_{aq,i,j} - \hat{C}_{aq,i,j})^2 \to \min$$
(8)

The standard deviation (SD) (σ_i) for each parameter is evaluated through Eq (9) [42, 43]. Here, x² stands for the RSSQ denoting the difference between the calculated and experimental data, while N represents the total number of experimental data points and P is the parameter count. Symbol m_{ii} -1 indicates the ith diagonal element found in the inverse matrix M, as defined in Eq (10), with a_i representing the parameter estimated by the kinetic model. Eq (11) was used for computing the partial derivative of the fitting function, $\partial F_n/\partial a_i$. To precisely calculate these partial differential values, it is essential to select a small δ (where δ <<1), so in this study, a value of 10⁻⁴ a_i was applied to each parameter.

$$\sigma_i = \sqrt{\frac{m_{ii}^{-1} x^2}{N - P}} \tag{9}$$

$$m_{ij} = \sum_{n=1}^{N} \frac{\partial F_n}{\partial a_i} \times \frac{\partial F_n}{\partial a_j}$$
(10)

$$\frac{\partial F_n}{\partial a_i} = \lim_{\Delta a_i \to 0} \frac{\Delta F_n}{\Delta a_i} \approx \frac{F_n(a_i + \delta) - F_n(a_i)}{\delta}$$
(11)

219 The standard deviation for parameters like the adsorption equilibrium coefficient (K), which is derived 220 indirectly by dividing the adsorption rate coefficient (k_1) by the desorption rate coefficient (k_2) , can be 221 calculated using Eq (12). In this equation, a and b denote the estimated parameters (specifically, k_1 and 222 k_2), while σ represents the associated standard deviation.

$$\sigma(\frac{a}{b}) = \sqrt{\left(\frac{\sigma(a)}{a}\right)^2 + \left(\frac{\sigma(b)}{b}\right)^2} \tag{12}$$

223 A parameter is considered to hold statistical significance if its estimated value surpasses its 224 corresponding standard deviation [42, 43]. Hence, the standard deviation was computed for all estimated parameters and used to ascertain the significance of each estimation offered by the model. 225

226 3. Results and discussion

227 Table 1 contains a comprehensive list of all the experiments conducted on the photocatalytic 228 degradation of ethanol and acetaldehyde. In order to allow the compounds to adsorb onto the catalyst 229 surface and reach equilibrium, the first 15 minutes of each experiment were carried out without light 230 irradiation. All experiments were performed at least as duplicate in order to ensure the reproducibility of 231 the results and to yield the standard deviation for the associated figures.

232

3.1 Catalyst characterization

233 This section presents a brief summary of the characterization results of the reduced catalyst (R-ZnO) in 234 reference to the commercial catalyst. A comprehensive characterization can be found in our previous study 235 [24].

236 To investigate the reducibility of the C-ZnO catalyst, the H2-TPR profile of C-ZnO is derived based on 237 TPR analysis (Figure S.4a). The TPR profile of the catalyst shows several Gaussian peaks at different temperatures representing various oxygen bonds with different strengths on the catalyst's surface. As the 238 239 reduction temperature rises, a greater quantity of oxygen vacancies is generated to potentially influence 240 the photocatalytic performance of ZnO [44, 45]. The concentration of oxygen vacancies produced by 241 hydrogen reduction was quantified using pulse chemisorption oxidation (PCO) analysis. Figure S.4b shows that C-ZnO has a low concentration of 1.33 10⁻⁵ mol gcat⁻¹ oxygen vacancies prior to reduction. After 242 reduction at 500 °C, the concentration of oxygen vacancies significantly increases to 3.99 10⁻⁵ mol gcat⁻¹. 243 244 XPS analysis was conducted on the catalyst before and after hydrogen reduction and all XPS spectra 245 were referenced to C 1s at 285 eV. Figure S.5 a and b show the O 1s spectrum of C-ZnO and R-ZnO, 246 respectively, with three distinct components: lattice oxygen (O_{lat} at 530 eV), oxygen vacancy (O_{vac} at 531 247 eV), and adsorbed oxygen (O_{ads} at 532 eV) [46, 47]. The results show effective reduction of the catalyst 248 with an increase in the ratio of oxygen vacancy to lattice oxygen from 0.44 in C-ZnO to 0.57 in R-ZnO 249 after hydrogen reduction. The maximum valence band of the catalysts was estimated from the surface XPS 250 spectrum data between -3 and 20 eV to investigate the electrical conductivity of the samples [48, 49]. 251 Figure S.6 compares the estimated valence band of C-ZnO and R-ZnO. The introduction of oxygen 252 vacancies to the catalyst resulted in an upward shift of the maximum valence band from 2.43 eV in C-ZnO 253 to 2.62 eV in R-ZnO. A greater maximum valence band of a photocatalyst indicates an increased capacity 254 for electron-holes to carry out oxidation [50]. Additionally, a higher maximum valence band can lead to a 255 higher generation rate of hydroxyl radicals in a photocatalytic process [51, 52].

The presence of oxygen vacancies was investigated using EPR analysis. Figure S.7a shows the EPR spectra of C-ZnO and R-ZnO catalysts. A symmetrical signal at g = 1.96, seen from both catalysts, indicates a trapped photo-generated electron on the zinc atom [53, 54]. However, only R-ZnO shows an additional smaller signal at g = 2.01 to reflect the presence of oxygen vacancies [55-57].

The XRD spectra of the C-ZnO and R-ZnO catalysts were examined to confirm the fine particle size and appropriate crystallinity [58], see Figure S.7b. The crystalline sizes of C-ZnO and R-ZnO were determined as 6.2 nm and 6.0 nm using the Williamson-Hall equation, and 5.3 nm and 5.4 nm employing the Scherrer equation in our prior study [24]. The high quality of the crystal structure of R-ZnO catalyst, as confirmed by the occurrence of sharp and narrow peaks, suggests its stability during the hydrogen reduction process. The major peaks observed at $2\theta \approx 31.8^{\circ}$, 34.5° , and 36.3° in the spectrum were identified as (100), (002), and (101) lattice planes, respectively [59, 60]. The results are consistent with the standard JCPDS for ZnO [61].

268 According to BET analyses, the surface area and total pore volume of R-ZnO were found to increase 269 significantly through the introduction of new oxygen vacancies on its surface compared to C-ZnO [62]. 270 The surface area of R-ZnO increased from $43.0 \pm 0.1 \text{ m}^2/\text{g}$ to $48.3 \pm 0.1 \text{ m}^2/\text{g}$, while the total pore volume 271 increased from 8.87 10^{-2} cm³/g to 1.06 10^{-1} cm³/g. The effect of oxygen vacancies on the bandgap of the 272 catalyst was investigated using the Tauc plot method [63, 64]. As shown in Figure S.8a, a significant red 273 shift was observed in the Tauc plot of the catalyst after hydrogen reduction. Consequently, the bandgap of 274 R-ZnO was lowered down to 3.09 eV from 3.24 eV in the C-ZnO catalyst. This suggests that the creation 275 of oxygen vacancies in the R-ZnO catalyst has improved photon harvesting potential towards visible light 276 [65].

The creation of oxygen vacancies was also evaluated using photoluminescence (PL) analysis. In the PL spectra shown in Figure S.8b, the peak at 380 nm observed in C-ZnO corresponds to the transition of electrons from the valence to the conduction bands of ZnO [66]. However, in R-ZnO catalyst, the same peak experiences a red shift to 421 nm due to the changes in its crystal structure caused by hydrogen reduction [67]. This shift is in agreement with the reduction-induced decrease of the estimated bandgap of the catalysts by Tauc plot. Additionally, the broad peak observed at 663 nm in the R-ZnO catalyst indicates the presence of oxygen vacancies where the recombination of electron-hole pairs can take place [68, 69].

3.2 Ceramic filter coating

285 To investigate the effectiveness of the catalyst coating on the ceramic filters, FE-SEM and EDS analysis 286 were performed on plain ceramic filters and ceramic filters coated with C-ZnO and R-ZnO catalysts. As 287 illustrated in Figure 2a and b, the uncoated filter has a smooth surface. The EDS analysis revealed that the 288 surface of the uncoated filter consists of 28.8 wt% silicon, 12.4 wt% carbon, 8.3 wt% aluminum, and 50.3 289 wt% oxygen, in line with the material specifications (silicon carbide and aluminum oxide) provided by the 290 manufacturer. Figure 2c to f show the FE-SEM and EDS images of the ceramic filter coated with C-ZnO 291 and R-ZnO. It is evident from the images that a uniform layer of nanoparticles has been successfully 292 deposited onto the surface of the ceramic filter. Additionally, the hydrogen reduction process did not 293 significantly affect the morphology of the R-ZnO nanoparticles, compared to that of C-ZnO. Using these 294 FE-SEM data, the average particle size of the C-ZnO and R-ZnO catalysts coated on the ceramic filters 295 are 45 nm and 42 nm respectively. EDS analysis of C-ZnO (Figure 2d) revealed a weight percentage of 296 26.5% oxygen and 73.5% zinc. In contrast, the EDS analysis of R-ZnO (Figure 2f) showed a reduction in 297 weight percentage of oxygen to 22.1% and an increase in zinc to 77.9%. This reduction in oxygen 298 percentage is likely due to the hydrogen reduction process [70].

299 To investigate the reproducibility of the ceramic filter coating, three plain filters were coated with 500 mg of C-ZnO to give a coating density of 10.20 mg cm⁻² (mg of catalyst per square centimeter of 300 301 coated filter) and used in photocatalytic experiments at an initial ethanol concentration of 5 ppm (volume 302 basis), see Figure 3a. During the first 15 minutes of the experiment (under the dark condition), the 303 concentration of ethanol decreased due to adsorption until it reached equilibrium, while the concentration 304 of acetaldehyde did not increase. Once the lights were turned on, the photocatalytic degradation of ethanol 305 started, leading to the production of acetaldehyde. The concentration of acetaldehyde increased until 306 equilibrium at around 50 minutes from the start of the experiment, at which point the rate of production of 307 acetaldehyde was equal to the rate of its photocatalytic degradation. Afterward, the concentration of 308 acetaldehyde declined since the concentration of ethanol had significantly decreased, and less acetaldehyde 309 was being produced than degraded. The almost identical experimental results of the three different filters 310 (standard deviation less than 2%) support the reproducibility of the ceramic filter coating.

311 In order to optimize the mass of catalyst used for coating a ceramic filter, three different filters were coated with 125, 250, and 500 mg of C-ZnO, to give coating densities of 2.55, 5.10, and 10.20 mg cm⁻², 312 313 respectively. These filters were then used for photocatalytic degradation of ethanol, as shown in Figure 3b. 314 The adsorption removal (dark phase, after 15 minutes) increased from 19.9% to 31.2%, as the mass of the 315 coated catalyst increased from 125 mg to 250 mg. Moreover, during the photocatalytic removal process, 316 the filter with 250 mg of coated catalyst showed a faster degradation of both ethanol and acetaldehyde. 317 The increase in coated catalyst mass from 125 mg to 250 mg allowed for more nanoparticles to stabilize 318 on the surface and cover the ceramic filter more effectively, improving the photocatalytic efficiency of the 319 filter. However, when the mass of the coated catalyst was further increased to 500 mg, the photocatalytic 320 degradation rate remained almost equal to the filter coated with 250 mg of catalyst, despite a slight increase 321 in the adsorption removal to 35.0%. The most plausible reason for this is that, as the mass of coated catalyst 322 increased, the nanoparticles started to pile up on top of each other and form a multi-layer. Since the ZnO 323 nanoparticles are porous material, the ethanol molecules were still able to reach the lower layers, which 324 slightly increased ethanol adsorption [71]. However, the UV light could not penetrate the bottom layers of 325 the nanoparticles, resulting in a constant photocatalytic degradation rate [72]. In conclusion, increasing the 326 coating mass of the catalyst to 500 mg did not result in a higher photocatalytic degradation rate, and a 327 catalyst mass of 250 mg was selected as the optimum coating mass in our setup.

In order to investigate the impact of the air purifier flow rate on the photocatalytic process, three experiments were conducted with different fan speeds: low (100 L/min), medium (130 L/min), and high (160 L/min) flow rate. Figure S.9 in the Supplementary Information depicts the effect of the air purifier fan speed on the ethanol photocatalytic degradation. The findings demonstrate that the flow rate of the air purifier's fan does not significantly affect the photocatalytic process (standard deviation less than 2%), indicating efficient air mixing within the reactor. As a result, the medium fan speed (130 L/min) was chosen for the remaining photocatalytic experiments, and a uniform mixing of air and the photocatalyst within the reactor was assumed for kinetic modeling.

336 3.3 Kinetic modeling and the effect of relative humidity

337 Figure 4 presents the outcomes of the photocatalytic ethanol degradation experiments at different 338 relative humidity (RH). The dots on the graph represent the experimental data, while the lines denote the 339 calculated data using Eqs (1) to (8) of the kinetic model. The results reveal that the adsorption removal of 340 ethanol reduces significantly with increasing RH. Specifically, the highest adsorption removal of ethanol 341 by C-ZnO catalyst is 40.8% at 5% RH, while it drops to 7.1% at 75% RH. Similarly, the adsorption removal 342 by R-ZnO at 5% and 75% RH is 49.2% and 10.2%, respectively. The rise in RH causes an increase in 343 water vapor pressure, which increases the adsorption of water on the ZnO nanoparticles due to their high 344 hydrophilicity [73, 74]: see Eq (5). This promotes more active sites to be occupied by water molecules and 345 cause a lower adsorption removal of ethanol.

In order to gain a more comprehensive insight into the photocatalytic process and to improve the accuracy of curve fitting to the experimental data, additional experiments were conducted at an initial ethanol concentration of 10 ppm. Figure 5 illustrates a comparison of the results obtained with initial concentrations of 10 ppm and 5 ppm, using both the C-ZnO and R-ZnO catalysts. It is apparent from the results that R-ZnO records a higher removal efficiency and photocatalytic degradation rate at both initial concentrations. Moreover, R-ZnO also exhibits a faster photocatalytic degradation rate for acetaldehyde. 352 Table 2 summarizes the estimated kinetic parameters. The results show that the value of $k_{1,E}$, representing the adsorption rate of ethanol, increases from $(3.64 \pm 0.16) 10^4$ (g mol⁻¹ min⁻¹) for C-ZnO to 353 (3.85 ± 0.12) 10⁴ (g mol⁻¹ min⁻¹) for R-ZnO, indicating a higher adsorption rate on the catalyst after 354 355 hydrogen reduction. Conversely, the estimated value of $k_{2,E}$, representing the desorption rate, drops from $(3.96 \pm 0.21) 10^{-3}$ (g L⁻¹ min⁻¹) for C-ZnO to $(3.41 \pm 0.13) 10^{-3}$ (g L⁻¹ min⁻¹) for R-ZnO, indicating a lower 356 desorption rate for the reduced catalyst. The adsorption equilibrium coefficient, K_{ad,E}, defined as the ratio 357 of k_{1,E} to k_{2,E}, shows a higher affinity of ethanol for the reduced catalyst with significant increase in its 358 value from $(9.19 \pm 0.07) \ 10^6$ (L mol⁻¹) in C-ZnO to $(1.13 \pm 0.05) \ 10^7$ (L mol⁻¹) in R-ZnO. This can be 359 360 attributed to the creation of surface oxygen vacancies at the surface of R-ZnO, which can act as active sites 361 for the adsorption of ethanol molecules [75]. This finding is consistent with the observed increase in the estimated values of C_{tot} , from (7.34 ± 0.02) 10⁻⁶ (mol g⁻¹) in C-ZnO to (8.86 ± 0.02) 10⁻⁶ (mol g⁻¹) in R-362 363 ZnO. It should be noted that the increased adsorption of ethanol by R-ZnO is the most pronounced at 5% 364 RH. This is because at high RH levels, similar to ethanol, water molecules also tend to be adsorbed in higher quantities on the R-ZnO catalyst. Evidence of this is shown by a higher estimated value of k_w, (8.09 365 \pm 0.04) 10⁻¹ (kPa⁻¹) for R-ZnO, compared to (7.70 \pm 0.04) 10⁻¹ (kPa⁻¹) for C-ZnO. 366

The estimated values for b, which represents the average number of water molecule layers adsorbed on the surface of the catalyst, are consistent with this observation. Specifically, for C-ZnO, the b values increase from 0.85 ± 0.12 at 5% RH to 1.99 ± 0.03 at 75% RH. Similarly, for R-ZnO catalyst, the b values for 5% and 75% RH are estimated to be 0.97 ± 0.27 and 2.08 ± 0.03 , respectively. These findings suggest that as RH increases, the number of water molecule layers on the catalyst surface also increases significantly. The average number of layers of ethanol and acetaldehyde (parameter a) adsorbed on C-ZnO and R-ZnO is estimated as 2.12 ± 0.04 and 2.15 ± 0.03 , respectively. Note that this parameter is assumed to be constant across all RH levels as the initial concentration of ethanol and acetaldehyde is the same inall experiments.

376 To obtain a more precise understanding of the adsorption and photocatalytic degradation behavior of acetaldehyde, experiments were conducted at the same RH and at an initial acetaldehyde concentration of 377 378 5 ppm, without the presence of ethanol. The experimental and calculated data for the adsorption and 379 photocatalytic degradation of acetaldehyde are shown in Figure 6. It can be observed that the removal of 380 acetaldehyde through adsorption is significantly lower than that of ethanol. Similar to the results for 381 ethanol, an increase in RH from 5% to 75% resulted in a decrease of the adsorption removal of 382 acetaldehyde, from 5.2% to 1.9% with C-ZnO and from 6.5% to 2.4% with R-ZnO. The estimated values of the parameters $k_{1,A}$ and $k_{2,A}$, which represent the adsorption and desorption rates of acetaldehyde, are 383 $(2.57 \pm 0.29) 10^4$ (g mol⁻¹ min⁻¹) and $(3.78 \pm 0.48) 10^{-2}$ (g L⁻¹ min⁻¹) respectively for C-ZnO, while the 384 values are $(2.69 \pm 0.33) 10^4$ (g mol⁻¹ min⁻¹) and $(3.78 \pm 0.46) 10^{-2}$ (g L⁻¹ min⁻¹) for R-ZnO, respectively. 385 The acetaldehyde adsorption equilibrium coefficient, $K_{ad,A}$, can be calculated as (6.82 ± 0.17) 10⁵ (L mol⁻ 386 ¹) for C-ZnO and $(7.11 \pm 0.17) \ 10^5$ (L mol⁻¹) for R-ZnO, which is two orders of magnitude lower than 387 388 those of ethanol. This can be attributed to the lower polarity of acetaldehyde than ethanol, primarily since 389 acetaldehyde has no hydroxyl functional group [76]. The high hydrophilicity of the ZnO catalyst causes it 390 to preferentially adsorb molecules with hydroxyl functional groups [77, 78].

Figure 7 illustrates the possible photocatalytic reactions and degradation pathway of ethanol. Under UV-A light, an electron in the valence band of ZnO is excited to the conduction band, leaving a hole in the valence band behind [79]. The excited electron can react with an oxygen molecule in air, producing superoxide radicals [80]. The hole can react with a water molecule in the air, producing hydroxyl radicals [81, 82]. These superoxide and hydroxyl radicals can then react with ethanol molecules in the air to yield acetaldehyde with degradation rates represented by $k_{3,E}$ and $k_{4,E}$, respectively. The values of $k_{3,E}$ and $k_{4,E}$

for C-ZnO are estimated as $(2.55 \pm 0.27) \ 10^{-3} \ (\text{min}^{-1})$ and $2.63 \pm 0.14 \ (\text{L mol}^{-1} \ \text{min}^{-1})$, respectively. The 397 corresponding values for R-ZnO increased to $(4.31 \pm 0.33) 10^{-3} (\text{min}^{-1})$ and $2.76 \pm 0.20 (\text{L mol}^{-1} \text{min}^{-1})$, 398 399 respectively. This increase can be attributed to the presence of oxygen vacancies in R-ZnO that result in a 400 higher maximum valence band [51, 52]. Furthermore, the estimated parameters of k_{3,EA} and k_{4,EA} are 401 exactly equal to k_{3.E} and k_{4.E} for both catalysts, as all ethanol degradation in the gas phase resulted in the 402 production of acetaldehyde before further mineralization to water and CO₂. To further degrade the 403 produced acetaldehyde in the gas phase, it can react with superoxide radicals (with a degradation 404 coefficient of $k_{3,A}$) or hydroxyl radicals (with a coefficient of $k_{4,A}$) to form water and CO₂. Alternatively, 405 it may adsorb to the surface of the catalyst and follow a degradation path as surface reactions. The estimated parameters ($k_{3,A}$ and $k_{4,A}$) for C-ZnO are (9.67 ± 0.09) 10⁻⁵ (min⁻¹) and (1.02 ± 0.22) 10⁻³ (L mol⁻¹ min⁻¹), 406 while those for R-ZnO are $(1.09 \pm 0.09) \ 10^{-4} \ (\text{min}^{-1})$ and $(1.24 \pm 0.55) \ 10^{-3} \ (\text{L mol}^{-1} \ \text{min}^{-1})$, respectively. 407 408 These values indicate that R-ZnO has higher degradation coefficients for acetaldehyde, similar to the trend 409 observed for ethanol's degradation coefficients.

410 Surface reactions involve the direct reaction between the adsorbed compound and the photo-induced 411 electron-holes at the catalyst's surface. In an alternative scenario, an adsorbed oxygen molecule may react 412 with electron-holes on the catalyst's surface, giving rise to a superoxide radical [83-85]. This radical can 413 further engage with adsorbed compounds, leading to degradation at the catalyst's surface. Because of 414 constant concentration of the electron-holes and oxygen during all experiments, these reactions are combined and represented by $k_{5,E}$, which is estimated to be $(1.79 \pm 0.09) 10^{-2} (min^{-1})$ and $(2.26 \pm 0.12) 10^{-1}$ 415 ² (min⁻¹) for C-ZnO and R-ZnO, respectively. The higher value in R-ZnO can be due to a higher maximum 416 417 valence band caused by the presence of oxygen vacancies, which can enhance the oxidative ability of the photo-generated electron-holes [50]. Another parameter, k_{6.E}, represents the photocatalytic reaction 418 419 between the adsorbed ethanol and the hydroxyl radicals at the catalyst's surface. The estimated values for 420 $k_{6,E}$ are (2.35 ± 0.05) 10⁴ (g mol⁻¹ min⁻¹) for C-ZnO and (2.42 ± 0.05) 10⁴ (g mol⁻¹ min⁻¹) for R-ZnO. This 421 parameter follows the same trend as $k_{5,E}$, as the higher maximum valence band of R-ZnO can increase the 422 hydroxyl production rate due to the more active photo-generated electron-holes [86]. Additionally, a higher 423 number of water molecules are adsorbed at the surface of R-ZnO catalyst, resulting in a higher production 424 of hydroxyl radicals.

425 Similarly to the parameters of acetaldehyde production in the gas phase (k_{3,EA} and k_{4,EA}), the estimated 426 values of k_{5.EA} and k_{6.EA} are equal to k_{5.E} and k_{6.E} in C-ZnO. This suggests that all of the ethanol adsorbed 427 on the surface of C-ZnO is oxidized to acetaldehyde. However, in the case of R-ZnO, although the estimated value for $k_{6,EA}$ is equal to $k_{6,E}$, the estimated value for $k_{5,EA}$ (1.61 ± 0.15) 10⁻² (min⁻¹) is lower 428 429 than that of $k_{5,E}$ (2.26 ± 0.12) 10⁻² (min⁻¹). This indicates that, at the R-ZnO surface, all ethanol molecules 430 reacting with hydroxyl radicals are converted to acetaldehyde before complete mineralization to water and 431 CO₂. However, a fraction of the ethanol molecules that react with electron-holes on the catalyst's surface 432 does not produce acetaldehyde. In this pathway, ethanol may degrade into smaller compounds and remain 433 on the catalyst's surface until they undergo complete mineralization to water and CO₂. The possibility of 434 production of by-products such as acetic acid and formic acid at the surface of the catalyst has been 435 reported [21, 87, 88]. This behavior can be attributed to the higher oxidative ability of photo-induced 436 electron-holes in R-ZnO, which is due to the upward shift in its maximum valence band [50-52].

The investigation into the potential production of acetic acid as a by-product during ethanol degradation was extended using both the kinetic model and experimental data on carbon balance (see section S.7 of the Supplementary Information). Figure S.10a illustrates the impact of relative humidity on acetic acid production, employing Eq (S.10) with the parameters from Table 2. The percentage of total ethanol moles converted to acetic acid decreases from 11.9% at RH 5% to 1.0% at RH 75%. These findings suggest that acetic acid production is more noticeable in the absence of hydroxyl radicals. In order to experimentally investigate the presence of acetic acid in the reactor, a carbon balance study was conducted using Eqs (S.11) and (S.12). Due to increased acetic acid production at low humidity levels, investigations were performed at RH 5% and 25%. Figure S.10b and c show deviations from carbon balance at these humidity levels. After light activation, both scenarios revealed a shortfall in expected carbon, indicating acetic acid production, with maximum deviations of 7.2% and 2.9% for RH 5% and 25%, respectively. Considering minimal acetic acid production, especially at higher indoor humidity levels, this by-product is omitted in the kinetic model.

450 The acetaldehyde molecules produced by the oxidation of ethanol at the surface of the catalyst can 451 further degrade to water and CO_2 by the electron-holes (represented by $k_{5,A}$) or the hydroxyl radicals (represented by $k_{6,A}$) at the catalyst surface. The estimated values for $k_{5,A}$ and $k_{6,A}$ are (1.40 ± 0.07) 10⁻¹ 452 (\min^{-1}) and (4.13 ± 0.24) 10⁴ (g mol⁻¹ min⁻¹) in C-ZnO, and (1.90 ± 0.08) 10⁻¹ (min⁻¹) and (4.36 ± 0.23) 10⁴ 453 $(g \text{ mol}^{-1} \text{ min}^{-1})$ in R-ZnO, respectively. Similar to ethanol, the estimated $k_{5,A}$ and $k_{6,A}$ are higher for R-ZnO 454 455 due to the presence of oxygen vacancies, resulting in a higher oxidative ability. Alternatively, the produced 456 acetaldehyde at the surface of the catalyst can also desorb into the air and follow one of the degradation 457 paths in the air.

458 **3.4 Quantification of each degradation pathway**

To assess the contributions of the individual degradation pathways to the overall degradation of ethanol and acetaldehyde, the proportion of reactions facilitated by each coefficient (k₃, k₄, k₅, and k₆) was calculated using equations (13) to (16) in conjunction with the estimated parameters outlined in Table 2. The corresponding values for acetaldehyde were computed using the same equations and the respective parameters of acetaldehyde, as represented in Eqs (S.13) to (S.16) in the Supplementary Information.

$$Ethanol_{by k_{3,E}} = \int_{t=0}^{t=180} V k_{3,E} C_{g,E} \xi dt$$
(13)

$$Ethanol_{by \ k_{4,E}} = \int_{t=0}^{t=180} V k_{4,E} \ C_{g,E} \ C_{g,w} \ \xi \ dt \tag{14}$$

$$Ethanol_{by k_{5,E}} = \int_{t=0}^{t=180} m_{cat} k_{5,E} C_{ad,E} \xi dt$$
(15)

$$Ethanol_{by k_{6,E}} = \int_{t=0}^{t=180} m_{cat} k_{6,E} C_{ad,E} C_{ad,w} \xi dt$$
(16)

464 Figure 8a and b depict the proportion of ethanol and acetaldehyde degraded by individual reaction coefficients in photocatalytic experiments employing R-ZnO at varying RH levels. The results for C-ZnO 465 466 are shown in Figure S.11. Notably, the reaction coefficients $k_{3,E}$ and $k_{4,E}$, representing gas-phase 467 degradation of ethanol, exhibit a lower impact, accounting for an average of 14.4% of the total degradation. 468 In contrast, the surface reactions denoted by $k_{5,E}$ and $k_{6,E}$ play a more significant role. The contribution of parameter k_{3,E} attributed to the ethanol degradation (in R-ZnO), as calculated by Eq (13), reaches its lowest 469 470 value of 0.11 µmol at RH 25% but peaks at 0.40 µmol at RH 75%. This variation is primarily due to the 471 Cg,E variable in Eq (13), which has its lowest values at RH 25% and its highest values at RH 75% (see 472 Figure 4). For acetaldehyde, the corresponding values of degradation by $k_{3,A}$ increase from 0.09 µmol at 473 RH 5% to 0.17 µmol at RH 75%. The portion of k_{4,E} in ethanol degradation rises from 0.01 µmol at RH 474 5% to 0.24 µmol at RH 75%. Similarly, the corresponding values of k_{4,A} for acetaldehyde degradation 475 increase from 0.01 µmol at RH 5% to 0.18 µmol at RH 75%. As outlined in Eq (14), the increase in relative 476 humidity and C_{g,w} leads to a substantial increase in the quantity of ethanol (and acetaldehyde) degraded in 477 the gas phase.

The contribution of $k_{5,E}$ to ethanol degradation decreases from 0.87 µmol at RH 5% to 0.07 µmol at RH 75%. This decline is attributed to the only variable in Eq (15), which is the concentration of adsorbed ethanol ($C_{ad,E}$). The contribution of $k_{5,E}$ is notably higher at lower humidity levels, where $C_{ad,E}$ increases due to the absence of water molecules on the catalyst's surface. Figure 8c provides an illustration of the calculated values of adsorbed ethanol by R-ZnO at various humidity levels, computed through numerical integration of Eq (2). During the initial 15 minutes of dark adsorption, the ethanol concentration at the catalyst surface experiences a rapid increase, reaching its peak at equilibrium. Subsequently, upon exposure to UV light, the concentration of adsorbed ethanol drops due to photocatalytic degradation. It is evident that the concentration of adsorbed ethanol significantly rises at lower RH levels, leading to a greater contribution of k_{5,E} in ethanol degradation. Likewise, the corresponding values for acetaldehyde degradation by k_{5,A} decrease from 1.29 μ mol at RH 5% to 0.22 μ mol at RH 75%.

489 The portion of ethanol degradation attributed to $k_{6,E}$ is determined using Eq (16). As RH is increased 490 from 5% to 25%, the degraded ethanol increases from 1.07 µmol to 1.72 µmol. However, with a further 491 increase in RH to 75%, the contribution of this parameter declines to 1.36 µmol. As outlined in Eq (16), 492 k_{6.E} relies on both the concentrations of adsorbed ethanol and water (C_{ad.E} and C_{ad.w}). Figure 8d illustrates 493 the concentration of adsorbed water on the surface of R-ZnO, computed using Eq (5). As RH levels rise, 494 the concentration of adsorbed water increases substantially, while the concentration of adsorbed ethanol 495 decreases (Figure 8c). Consequently, the influence of k_{6,E} reaches its peak at RH 25%. It is noteworthy 496 that during the dark adsorption phase, ethanol adsorbs onto the catalyst's surface, occupying the available 497 active sites. Consequently, the concentration of water decreases until it reaches an equilibrium with the 498 adsorbed ethanol. Essentially, ethanol displaces water molecules from the catalyst's surface. Similar results 499 have been previously reported [76, 89]. At RH of 5%, the concentration of adsorbed water exhibits no 500 significant decrease. This phenomenon is because at low humidity levels, an ample number of unoccupied 501 active sites are available for ethanol adsorption. Consequently, there is no necessity to displace the 502 adsorbed water molecules. Upon exposure to UV light and the subsequent photocatalytic degradation of 503 ethanol, the concentration of adsorbed water on the catalyst's surface returns to its equilibrium values 504 before ethanol was introduced. In the case of acetaldehyde degradation, the contribution of k_{6.A} rises from 505 0.34 µmol at RH 5% to 1.21 µmol at RH 50%, and then declines to 0.88 µmol at RH 75%.

As illustrated in Figure 8a, the predominant oxidation of ethanol occurs through the $k_{5,E}$ and $k_{6,E}$ coefficients located on the catalyst's surface. However, the adsorption equilibrium coefficient for acetaldehyde, denoted as $K_{ad,A}$ (7.11 ± 0.17) 10⁵ (L mol⁻¹), is markedly lower than that of ethanol, $K_{ad,E}$ (1.13 ± 0.05) 10⁷ (L mol⁻¹). This disparity implies that acetaldehyde generated on the catalyst's surface cannot persist there for further oxidation into smaller molecules. To mathematically demonstrate this phenomenon and gain a deeper insight into the changes in acetaldehyde adsorption/desorption during the process, Eq (17) was plotted as a function of time.

$$\frac{dC_{ad,A}}{dt} = +V(k_{1,A}C_{g,A}C_* - k_{2,A}C_{ad,A})$$
(17)

513 Figure 9 depicts the quantity of acetaldehyde adsorbed (positive values) or desorbed (negative values) 514 at the surface of the R-ZnO catalyst, as calculated using Eq (17). In the initial 15 minutes of the experiments 515 conducted in the absence of light, the plotted values remain at zero since there is no acetaldehyde present 516 in the system. However, upon activating the lights, the oxidation of ethanol commences at the catalyst's 517 surface, resulting in the plotted values reaching their maximum negative levels. This signifies the 518 desorption of acetaldehyde from the surface. Notably, similar to the predominant contributions of k_{5.E} and k_{6.E}, the highest desorption values for acetaldehyde are observed at RH 25% and 50%, indicating quantities 519 520 of 0.15 and 0.13 µmol g_{cat}⁻¹ min⁻¹, respectively.

521 Over time, the changes in adsorption-desorption behaviors converge to a point of equilibrium (Eq 522 (17)=0), where acetaldehyde production equates to its degradation. This marks a state of balance within 523 the system, with the quantity of acetaldehyde adsorbed being precisely matched by its desorption. 524 Continuing further, as ethanol concentrations decrease, acetaldehyde production nearly ceases, and only 525 its degradation occurs at the catalyst's surface. As the concentration of acetaldehyde on the catalyst's 526 surface diminishes, the number of unoccupied active sites increases, enabling the adsorption of new gaseous acetaldehyde. Consequently, the values calculated using Eq (17) become positive, indicating the
adsorption of acetaldehyde by the catalyst.

529

3.5 Performance evaluation by quantum yield and CADR

530 One practical approach for assessing the efficiency of various experimental conditions (different RH 531 levels in this study) in a photocatalytic degradation system is to compute the quantum yield (OY) [24, 37]. 532 QY, in this context, represents the ratio of degraded molecules (ethanol and acetaldehyde) to the incident 533 photons entering the solution during the degradation time [90]. However, in calculation of QY, it is crucial 534 to distinguish between molecules removed from the system through physical adsorption and those removed 535 via photocatalytic degradation [91]. The kinetic model developed in this study provides a precise means 536 to calculate the total number of molecules removed through photocatalytic degradation. To accomplish 537 this, the total quantity of degraded ethanol molecules was computed by numerical integration of Eqs (13) 538 to (16) between t = 0 to $t = t_{50}$. The parameter t_{50} corresponds to the moment at which 50% of the initial 539 ethanol molecules undergo degradation. The total values for acetaldehyde degradation during the same 540 time span were calculated by summing Eqs (S.13) to (S.16). The rationale behind selecting t_{50} as the upper 541 limit for QY calculations lies in the initial stages of the experiment, where ethanol concentrations are higher and variations in reaction rates among different RH levels are more distinct. Consequently, 542 543 comparing QY across different RH conditions is facilitated during this phase.

Figure 10 provides a comparison of the calculated QY for both C-ZnO and R-ZnO catalysts. When considering only ethanol degradation, the QY for the C-ZnO catalyst increases from 2.00 10⁻⁴ at RH 5% to 4.64 10⁻⁴ at RH 25%, followed by a drop to 1.77 10⁻⁴ molecules.photon⁻¹ at RH 75%. On the other hand, for the R-ZnO catalyst, the QY rises from 3.22 10⁻⁴ at RH 5% to 6.85 10⁻⁴ at RH 25% but then decreases to 2.50 10⁻⁴ molecules.photon⁻¹ at RH 75%. Remarkably, among all humidity levels, RH 25% exhibits the highest QY in both catalysts. The interplay between gas-phase and surface reactions at various humidity levels creates an environment where RH 25% emerges as the optimal humidity level for the photocatalytic degradation of ethanol and acetaldehyde. Furthermore, R-ZnO consistently exhibits higher QY values across all RH levels, underscoring the enhanced photocatalytic activity resulting from hydrogen reduction and the generation of oxygen vacancies in the catalyst.

554 It should be noted that OY encompasses not only the degradation of the target molecules but also 555 includes the degradation of the products in the reactor. To better understand the difference in considering 556 only the main target molecule and including product degradation in QY calculations, the total degraded 557 acetaldehyde during the time span for reaching 50% ethanol degradation (t₅₀) was calculated and then 558 considered in the QY calculations. The results reveal that when considering acetaldehyde degradation in experiments with C-ZnO, the QY increases from 2.43 10⁻⁴ at RH 5% to 5.53 10⁻⁴ at RH 25%, subsequently 559 dropping to 2.14 10⁻⁴ molecules.photon⁻¹ at RH 75%. Similarly, for R-ZnO, the values rise from 3.88 10⁻⁴ 560 at RH 5% to 8.25 10⁻⁴ at RH 25% and then decrease to 3.11 10⁻⁴ molecules.photon⁻¹ at RH 75%. Notably, 561 562 neglecting acetaldehyde degradation in QY calculations results in a significant omission, accounting for a 563 considerable percentage (19-24%) of the actual QY.

564 One of the critical factors influencing the QY is the mass of the catalyst employed within the system. 565 To account for this influence in the QY computations, the space-time yield (STY) is calculated by dividing 566 the QY by the mass of the catalyst (250 mg) [25, 37]. The maximum STY is calculated to be 2.21 10⁻⁶ and 567 3.30 10⁻⁶ molecules photons⁻¹ mg_{cat}⁻¹ at RH 25% for C-ZnO and R-ZnO, respectively. This demonstrates 568 that R-ZnO exhibits a higher STY value in comparison to C-ZnO due to the presence of oxygen vacancies, 569 highlighting its superior photocatalytic performance. Furthermore, the results show relatively high STY compared to the values reported in literature, which range from 6.43 10⁻¹³ to 3.88 10⁻⁶ molecules photons⁻ 570 1 mg_{cat}⁻¹ [25]. 571

Another commonly employed performance assessment metric for domestic air purifiers is the calculation of clean air delivery rate (CADR). The formula for determining CADR is represented by Eq (18), where V is the volume of the reactor, k_e is the experimental decay constant (min⁻¹), and k_n is the natural decay constant (min⁻¹) [92].

$$CADR = V(k_e - k_n) \tag{18}$$

As evident from the blank experiments presented in Figure S.3, there is no natural decay within the chamber. Therefore, k_n is assumed to be zero. The experimental decay rate, k_e , was computed using Eq (1), assuming that the lights were activated from the beginning of the experiment (ξ =1 at t=0). The highest achievable CADR value, calculated as 4.82 L.min⁻¹, was observed at RH 25%. It is important to emphasize that no adsorbent filter was employed in this study, and all calculated CADR values are attributed solely to the photocatalytic removal process.

582 **3.6 Reusability**

583 One of the most important catalyst properties is the ability to reuse it in consecutive experiments. To 584 investigate this property, a 250 mg R-ZnO coated ceramic filter was used again under the same conditions 585 as experiment 13 in Table 1. This filter was used in a total of 18 experiments, including 8 experiments with 586 different humidity levels, 8 experiments with an initial acetaldehyde concentration of 5 ppm, and 2 experiments with an initial ethanol concentration of 10 ppm. Figure 11a shows a comparison of the initial 587 588 experiment at a RH of 25% with the reusing test after 18 experiments. The results show no considerable 589 difference between the two experiments (standard deviation less than 2%), indicating that the catalyst's 590 performance remained constant.

591 Moreover, the ceramic filter was subjected to FE-SEM and EDS analyses after 18 reusing experiments. 592 As depicted in Figure 11b and c, a uniform layer of the R-ZnO catalyst remained on the surface of the 593 ceramic filter. The EDS analysis results indicate that the weight percentages of oxygen and zinc atoms on the surface of the nanoparticles are 22.5% and 75.7%, respectively, which is consistent with the results of the freshly characterized R-ZnO catalyst. However, the EDS results of the reused ceramic filter show the presence of 1.8% carbon, which can be residual degradation products of ethanol formed during the photocatalytic reactions.

598 4. Conclusions

2nO nanoparticles demonstrate high efficiency in the photocatalytic degradation of ethanol and acetaldehyde in the air. Introducing oxygen vacancies through hydrogen reduction enhances ZnO's photocatalytic properties, including adsorption capacity and ethanol degradation rate. Optimal hydrogen reduction conditions involve 500°C treatment with a 10% H₂/Ar gas stream. The drop-cast method stabilizes the catalyst on ceramic filter, with an optimum coating concentration of 250 mg (5.10 mg cm⁻²). Coated filters exhibit reproducibility, confirmed through FE-SEM and EDS analyses, and their performance remained unchanged after 18 experiments, indicating durability for long-term applications.

The photocatalytic process is notably affected by relative humidity (RH). An increase in humidity results in more water molecules adsorbing on the catalyst's surface, occupying active sites and hindering ethanol adsorption. The highest adsorption occurs at 5% RH, while the optimal photocatalytic degradation are observed at 25% RH, where increased water molecules lead to higher hydroxyl radical production. However, at 75% RH, photocatalytic degradation diminishes due to reduced ethanol adsorption and decreased surface reaction with electron-holes.

The kinetic model developed provides a detailed insight into the photocatalytic degradation of ethanol and acetaldehyde, accounting for gas-phase and surface reactions. It considers reversible adsorptiondesorption, assigning degradation coefficients to each pathway. According to the model results, gas-phase degradation contributes only 14% of the total degradation, emphasizing surface reactions' dominance. Presence of oxygen vacancies increased the concentration of active sites from (7.34 ± 0.02) 10⁻⁶ in C-ZnO to (8.86 ± 0.02) 10⁻⁶ mol g_{cat}⁻¹ in R-ZnO, boosting adsorption capacity. Moreover, hydrogen reduction elevates the adsorption equilibrium coefficient of ethanol and acetaldehyde by R-ZnO. Quantum yield (QY) calculations reveal that RH 25% yields the highest QY of 6.98 10⁻³ in C-ZnO and 1.04 10⁻² molecules photon⁻¹ in R-ZnO catalysts (factor 1.5 higher). R-ZnO consistently exhibits superior QY compared to C-ZnO at all humidity levels, emphasizing enhanced photocatalytic activity by introduction of oxygen vacancies.

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630 List of symbols

Roman symbols

а	Number of adsorbed layers of ethanol and acetaldehyde	-
bi	Number of adsorbed layers of water at humidity level i	-
C_{ad}	Concentration of adsorbate on the surface of the catalyst	mol g ⁻¹
C_g	Concentration of compounds in the gas phase	mol L ⁻¹
C*	Concentration of free active sites	mol g ⁻¹
C _{tot}	Total concentration of active sites	mol g ⁻¹
\mathbf{k}_1	Adsorption rate coefficient	g mol ⁻¹ min ⁻¹
k ₂	Desorption rate coefficient	g L ⁻¹ min ⁻¹
k3	Gas phase degradation rate coefficient by superoxide radicals	min ⁻¹
k4	Gas phase degradation rate coefficient by hydroxyl radicals	L mol ⁻¹ min ⁻¹
k5	Surface degradation rate coefficient by electron-holes	min ⁻¹
k ₆	Surface degradation rate coefficient by hydroxyl radicals	g mol ⁻¹ min ⁻¹
kw	Water adsorption coefficient	kPa ⁻¹
m _{cat}	Catalyst mass	g
n	Number of each experiment	-
Nj	Number of experimental data in each experiment	-
$\mathbf{P}_{\mathbf{W}}$	Water vapor pressure	kPa
S	Residual sum of squares	$mol^2 L^{-2}$
V	Volume of the reactor	L
Greek sy	mbols	

ξ	Light switch	-
σi	Standard deviation calculated for each parameter	-
Subscript	S	
А	Acetaldehyde	-
E	Ethanol	-
EA	Oxidation of ethanol to acetaldehyde	-
W	Water	-
Abbrevia	tions and acronyms	
BET	Brunauer-Emmett-Teller	-
CADR	Clean air delivery rate	L min ⁻¹
C-ZnO	Commercial zinc oxide	-
EDS	Energy-dispersive x-ray spectroscopy	-
EPR	Electron paramagnetic resonance	-
FE-SEM	Field-emission scanning electron microscopy	-
PCO	Pulse chemisorption oxidation	-
QY	Quantum yield	Molecules photon ⁻¹
RSSQ	Residual sum of squares	$mol^2 L^{-2}$
R-ZnO	ZnO reduced at 500°C	-
SD	Standard deviation	-
STY	Space-time yield	Molecules.photons ⁻¹ mg _{cat} ⁻¹
TPR	Temperature programmed reduction	-
XPS	X-ray photoelectron spectroscopy	-

632

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882Table 1. Summary of experimental conditions for the performed photocatalytic883experiments. All experiments are conducted at room temperature $(25 \pm 2 \ ^{\circ}C)$ in duplicate884and the error bars, representing the SD on the average value, are demonstrated in the885corresponding figures.

	- correspond	Coated	Ethanol	Acetaldehyde	Relative	Fan speed	D '
	Experiment	catalyst (mg)	C_0 (ppm)	C ₀ (ppm)	humidity (%)		Figure
_	1	Blank	5	0	25	Medium	S.3
	2	C-ZnO (500)	5	0	25	Medium	3
	3	C-ZnO (500)	5	0	25	Medium	3
	4	C-ZnO (500)	5	0	25	Medium	3
	5	C-ZnO (125)	5	0	25	Medium	3
	6	C-ZnO (250)	5	0	25	High	S.9
	7	C-ZnO (250)	5	0	25	Low	S.9
	8	C-ZnO (250)	5	0	25	Medium	3,4,5,10,S.9,S.10
	9	C-ZnO (250)	5	0	5	Medium	4,10,S.10
	10	C-ZnO (250)	5	0	50	Medium	4,10,S.10
	11	C-ZnO (250)	5	0	75	Medium	4,10,S.10
	12	R-ZnO (250)	5	0	5	Medium	4,8,9,10
	13	R-ZnO (250)	5	0	25	Medium	4,5,8,9,10,11
	14	R-ZnO (250)	5	0	50	Medium	4,8,9,10
	15	R-ZnO (250)	5	0	75	Medium	4,8,9,10
	16	C-ZnO (250)	10	0	25	Medium	5
	17	R-ZnO (250)	10	0	25	Medium	5
	18	C-ZnO (250)	0	5	5	Medium	6
	19	C-ZnO (250)	0	5	25	Medium	6
	20	C-ZnO (250)	0	5	50	Medium	6
	21	C-ZnO (250)	0	5	75	Medium	6
	22	R-ZnO (250)	0	5	5	Medium	6
	23	R-ZnO (250)	0	5	25	Medium	6
	24	R-ZnO (250)	0	5	50	Medium	6
	25	R-ZnO (250)	0	5	75	Medium	6
	26 (reuse)	R-ZnO (250)	5	0	25	Medium	11

Entry	Parameter	C-ZnO	R-ZnO
1	$k_{1,E}$ (g mol ⁻¹ min ⁻¹)	(3.64 ± 0.16) 10 ⁴	(3.85 ± 0.12) 10 ⁴
2	$k_{2,E}(g L^{-1} min^{-1})$	(3.96±0.21) 10 ⁻³	(3.41 ± 0.13) 10 ⁻³
3	$k_{3,E}(\min^{-1})$	$(2.55\pm0.27) 10^{-3}$	(4.31 ± 0.33) 10 ⁻³
4	$k_{4,E}(L mol^{-1} min^{-1})$	2.63±0.14	2.76±0.20
5	$k_{5,E}$ (min ⁻¹)	(1.79 ± 0.09) 10 ⁻²	(2.26±0.12) 10 ⁻²
6	$k_{6,E} (g mol^{-1} min^{-1})$	(2.35 ± 0.05) 10 ⁴	(2.42 ± 0.05) 10 ⁴
7	$k_{3,EA}$ (min ⁻¹)	(2.55±0.87) 10 ⁻³	(4.31±1.72) 10 ⁻³
8	$k_{4,EA} (L mol^{-1} min^{-1})$	2.63±0.79	2.76±0.49
9	k _{5,EA} (min ⁻¹)	(1.79±0.12) 10 ⁻²	(1.61±0.15) 10 ⁻²
10	$k_{6,EA} (g mol^{-1} min^{-1})$	(2.35 ± 0.05) 10 ⁴	(2.42 ± 0.05) 10 ⁴
11	$k_{1,A} (g mol^{-1} min^{-1})$	(2.57 ± 0.29) 10 ⁴	(2.69±0.33) 10 ⁴
12	$k_{2,A} (g L^{-1} min^{-1})$	(3.78 ± 0.48) 10 ⁻²	(3.78±0.46) 10 ⁻²
13	$k_{3,A}$ (min ⁻¹)	(9.67±0.09) 10 ⁻⁵	(1.09±0.09) 10 ⁻⁴
14	$k_{4,A} (L \text{ mol}^{-1} \min^{-1})$	(1.02 ± 0.22) 10 ⁻³	(1.24 ± 0.55) 10 ⁻³
15	k _{5,A} (min ⁻¹)	$(1.40\pm0.07) 10^{-1}$	$(1.90\pm0.08) 10^{-1}$
16	$k_{6,A} (g mol^{-1} min^{-1})$	(4.13±0.24) 10 ⁴	(4.36 ± 0.23) 10 ⁴
17	$k_{w} \left(k P a^{-1} \right)$	(7.70 ± 0.04) 10 ⁻¹	(8.09±0.04) 10 ⁻¹
18	$C_{tot} (mol g^{-1})$	(7.34 ± 0.02) 10 ⁻⁶	(8.86±0.02) 10 ⁻⁶
19	a	2.12±0.04	2.15±0.03

Table 2. Estimated parameters of the kinetic model for the photocatalytic degradation of
ethanol and acetaldehyde in air with C-ZnO and R-ZnO.

20	b (RH 5%)	0.85±0.12	0.97 ± 0.27
21	b (RH 25%)	1.68±0.04	1.42 ± 0.05
22	b (RH 50%)	1.55±0.09	1.62 ± 0.06
23	b (RH 75%)	1.99±0.03	2.08±0.03



Figure 1. Reactor setup. 1) Air purifier. 2) ZnO coated ceramic filter. 3) UV LED light. 4)
Air pump. 5) Mixing fan. 6) Humidity sensor 7) Injection valve. 8) Flushing valve. 9) Light
switch. 10) Sampling port. 11) Mass flow controller. 12) Discharge ion source and upstream
quadrupole. 13) Flow tube. 14) Ion collider and downstream quadrupole. 15) Computer.



Figure 2. FE-SEM (a, c, e) and EDS (b, d, f) images of the uncoated ceramic filter (a, b), the ceramic filter coated with 250 mg of C-ZnO (c, d), and the ceramic filter coated with 250 mg R-ZnO (e, f).







Figure 3. Ceramic filter coating optimization. a) Reproducibility of the coating process:
filter #1 (--), filter #2 (--), and filter #3 (--), using experimental conditions 2 to 4 in Table
b) optimization of the catalyst mass used for coating: 125 mg (--), 250 mg (--), and 500
mg (--) of C-ZnO using experimental conditions 4, 5, and 8 in Table 1.





912 Figure 4. Effect of relative humidity (RH) on adsorption and photocatalytic degradation

913 of ethanol by a) C-ZnO and b) R-ZnO. (●) RH 5%, (▲) RH 25%, (■) RH 50%, and (●)
914 RH 75%. Full lines are generated through the integration of Eqs (1) to (4), utilizing the

915 reaction conditions 8 to 15 outlined in Table 1 (along with parameter values specified in

916 **Table 2).**



919 **R-ZnO (blue)** at different initial concentrations of 5 and 10 ppm. (•) $C_0 = 5$ ppm with R-920 **ZnO, (** \bigstar **)** $C_0 = 5$ ppm with C-ZnO, (•) $C_0 = 10$ ppm with R-ZnO, and (•) $C_0 = 10$ ppm.

- 921 Full lines are generated through the integration of Eqs (1) to (4), utilizing the reaction
- 922 conditions 8, 13, 16, and 17, outlined in Table 1 (along with parameter values specified in





Figure 6. Effect of relative humidity (RH) on the adsorption and photocatalytic
degradation of acetaldehyde by a) C-ZnO and b) R-ZnO. (●) RH 5%, (▲) RH 25%, (■)
RH 50%, and (●) RH 75%. Full lines are generated through the integration of Eqs (3) and
(4), utilizing the reaction conditions 18 to 25 outlined in Table 1 (along with parameter
values specified in Table 2).



932 Figure 7. Photocatalytic degradation mechanism of ethanol and acetaldehyde with their

corresponding kinetic constants by R-ZnO catalyst.



Figure 8. The contribution of each reaction coefficient in photocatalytic degradation of
a) ethanol, b) acetaldehyde at (=) RH 5%, (=) RH 25%, (=) RH 50%, and (=) RH 75% by
R-ZnO. The concentration of adsorbed c) ethanol and d) water at the surface of R-ZnO
catalyst at (-) RH 5%, (-) RH 25%, (-) RH 50%, and (-) RH 75%. Data is generated
through the integration of Eqs (13) to (16), utilizing the reaction conditions from
experiments 12 to 15 outlined in Table 1 (along with parameter values specified in Table 2).

945 Figure 9. Changes in concentration of adsorbed acetaldehyde by R-ZnO. a) RH 5% (—),

946 b) RH 25% (---), c) RH 50% (---), and d) RH 75% (---). Data is generated by Eq (17),

947 utilizing the reaction conditions from experiments 12 to 15 outlined in Table 1 (along with

948 parameter values specified in Table 2).

949 950

Figure 10. Quantum yield calculations for a) C-ZnO and b) R-ZnO catalysts. (**a**) for only ethanol degradation till t₅₀ of ethanol, (**b**) for ethanol and acetaldehyde degradation. Data is generated from experiments 8 to 15 outlined in Table 1 (along with parameter values specified in Table 2).

Figure 11. a) Photocatalytic performance of R-ZnO catalyst after reusing for 18 experiments, (—) fresh R-ZnO, (—) reused R-ZnO, using experimental conditions 13 and 26 in Table 1. b) FE-SEM of the R-ZnO coated filter after reusing, c) EDS image of the R-ZnO coated filter after reusing.