



Influence of humidity on the removal of volatile organic compounds using solid surfaces



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ABSTRACT

In recent years, much attention has been devoted to understand how the humidity affects the volatile organic compound (VOC) removal efficiencies using absorbents, photocatalysts or dark-catalysts and both positive and negative effects of humidity on VOC removal have been reported. We show that sorption capability of VOCs of absorbents with high surface areas can be significantly reduced by the competitive adsorption with water in the air and, by hydrophobically modifying the absorbent surfaces, selective sorption of VOCs to water molecules is achieved. For the TiO₂ photocatalysts, humidity was found to have both positive and negative effects on catalytic activity; humidity facilitates the total oxidation of toluene to CO₂ allowing the long-term stability of the catalytic activity, on the other hand, reduces the adsorption of VOCs on the catalyst surface. By depositing TiO₂ islands on hydrophilic nanodiamond nanoparticles, positive effect of humidity becomes more pronounced. Positive and negative effects of humidity analogous to those on photocatalyst were also observed for the dark-catalysts, NiO nanoparticle decorated mesoporous silica. TiO₂ interlayer with a high affinity toward toluene was applied between SiO₂ and NiO and, as a result, negative effect of humidity, reduction of toluene adsorption in the presence on water, is suppressed.

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1. Introduction

Volatile organic compounds (VOCs) in the indoor as well as outdoor environments can be harmful to the human beings and therefore, remediation of the VOC level has been becoming more and more important issue in environmental science and technology. In the indoor environments, VOCs stem from some components of interior construction materials, in which organic solvents are included (e.g. paints) [1–3]. Also, VOCs can form during cooking in the kitchen [1–3]. Regarding external environments, VOCs can form from incomplete combustion of fuels in the industry and automobiles [4,5]. Among various VOCs benzene and its derivatives (e.g., toluene and xylene) were found to be detrimental to the human body and therefore, their concentration management has been becoming very important [3,4,6]. In addition, some VOCs are so toxic, that they can be even used as chemical warfare agents [7].

There are several different strategies to remove VOCs from the atmosphere [8–38]. The most widely used method for removing

VOCs is based on high-surface-area absorbents such as activated carbon, which can capture VOCs within micro and mesopores either by chemisorption or physisorption [9–16]. Alternatively, one can use photocatalysts, and typically TiO₂ is widely used due to its high photocatalytic efficiency and chemical stability [18–24]. In photocatalytic process, electrons and holes created in the semiconductive materials can interact with oxygen molecules or water, resulting in formation of strongly oxidizing agents (superoxide and hydroxyl (OH) radicals). These strongly oxidizing agents can then decompose organic molecules chemisorbed on the photocatalyst surface. TiO₂ can only absorb UV light, and this is considered to be a drawback of TiO₂-based photocatalysis and nowadays, much attention has been devoted to visible-light responsive photocatalysts [18,20,22]. One can also consider dark catalysts, which may need some heat for catalytic operation [25–38]. On catalytic surfaces, oxygen can dissociatively chemisorb, which can then oxidize chemisorbed VOC molecules. Also water molecules can be dissociatively chemisorbed on the surface, which can then form OH radicals. Note that the OH radicals can also participate in the oxidation of VOCs chemisorbed on the surface [25,30,33]. Generally, Pt-group metals are known to be active for VOC oxidation and recently, more economic solutions

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such as Ni, or Mn-based catalysts with various forms have been proposed [26,27,29,31–33,37–40].

In the atmosphere, water vapor almost always exists and therefore, influence of the water vapor on the performance of materials for VOC removal has been of much interest. For absorbent, water vapor can play a negative role due to the competitive interaction between water and VOCs in the absorbent [10,12,14–16]. As aforementioned, for photocatalysis, it is well known that one of the possible paths for the photocatalytic decomposition of organic molecules includes OH radicals, which can be formed via interaction of water molecules with holes created in the semi-conductive photocatalyst upon light-harvesting. It is worth mentioning that formation of OH radicals during photocatalytic processes under humid atmospheric conditions have been observed by laser-induced fluorescence, validating the aforementioned mechanism of photocatalytic decomposition of organic molecules [41,42]. Therefore, one could suggest that the humidity play a positive role for the oxidation of VOCs [19–22,24]. However, one should also take competitive adsorption between VOCs and water molecules on photocatalysts into account, which can be negative to the photocatalytic activity [17,19–24]. A similar argument can be also valid for dark catalysts; water molecules can form OH radicals, and play a positive role to the catalytic activity, however, competitive adsorption between water and VOCs could result in decrease of the catalytic activity for oxidation [25,28,30,33,34,43].

In the present work, some examples about how humidity can have influence on the VOC removal efficiency of absorbent, photocatalyst, and dark-catalyst are provided. We also show some examples how one can reduce the negative effects of humidity on the VOC removal efficiency either by using surface modification of absorbents and catalysts with thin film deposition, or synthesizing a novel structure with a resistance towards influence of water vapor.

2. Experimental

All the experiments were carried out in Sungkyunkwan University, Korea. Please refer to the original papers for the detailed description, since all the experimental methods are only briefly described here.

2.1. Sample preparation

For the hydrophobic surface modification of mesoporous silica and activated carbon fiber (ACF), polydimethylsiloxane (PDMS) vapor deposition technique was used [44,45]. Mesoporous silica and ACF was outgassed at 500 °C for 3 h and 300 °C for 3 h, respectively, and placed in a stainless steel chamber with fluidic PDMS. After sealing the chamber from the outside, the temperature of the chamber was increased to 300 °C and maintained for 16 h for mesoporous silica, while ACF was coated at 150 °C for 1 h.

TiO₂/nanodiamond, NiO/SiO₂ and NiO/TiO₂/SiO₂ catalysts were prepared using home-made atomic layer deposition (ALD) system [46,47]. For the deposition of TiO₂, titanium tetrakisopropoxide (Ti[OCH(CH₃)₂]₄, TTIP) and distilled water were used as titanium and oxygen source, respectively. The temperatures of TTIP and water bottles were kept at 50 °C or room temperature, respectively, and the sample was kept at 150 °C during the deposition. On the other hand, bis(cyclopentadienyl) nickel (Ni(Cp)₂) and O₂ were used as precursors for nickel and oxygen, respectively. During the deposition, the temperature of Ni(Cp)₂ and that of the sample were kept at 60 °C and 260 °C, respectively. One cycle of ALD process was achieved through following steps: [metal precursor exposing - N₂ purging - evacuation - oxygen precursor exposing - N₂ purging - evacuation]. Base pressure was kept below 10 mTorr and high

purity N₂ (99.999%) gas was used as purging gas between precursor exposing steps. Please refer to the original papers for the detailed deposition parameters [46,47].

2.2. Sample characterizations

For the determination of functional groups on the sample surfaces, Fourier transform infrared (FT-IR, Bruker, Optics/vertex 70) spectral analyses were carried out in a diffuse reflectance mode. Water contact angle on a surface was evaluated by using a Theta optical tensiometer (KSV Instruments, Ltd.) equipped with a digital camera connected to the computer and Young-Laplace curves were employed for the fitting method. Contact angle on sample surface was analyzed as continuously increasing the droplet volume and the maximum value was defined to be the advancing contact angle, whereas the minimum contact angle value obtained as reducing the droplet volume was defined as the receding contact angle. By subtracting the receding contact angle from the advancing contact angle, the contact angle hysteresis was determined.

The N₂ adsorption-isotherm at 77 K was used to evaluate the surface area and pore size distribution of samples based on the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses, respectively. The morphological images of samples were obtained with transmission electron microscopy (TEM, JEOL, JEM-3010) and elemental compositions of samples were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 720-ES, Agilent).

2.3. Absorption and desorption experiments

For the evaluation of pre-concentration ability of hydrophobized mesoporous silica and comparison with that of bare silica, hydrophobized and bare silica were outgassed and exposed to dimethyl methylphosphonate (DMMP) vapor under dry or humid (~80 RH%) conditions, respectively [44]. After the exposure for 24 h, only the absorbents were collected and transferred to the reactor connected to gas chromatography (GC, Aglient-6890N) and temperature programmed desorption (TPD) spectra were obtained for each sample by analyzing thermally desorbing molecules with GC. All the TPD experiments were carried out under a constant flow of nitrogen gas and the temperature of the reactor was increased from 30 to 630 °C at a ramping rate of 2 °C/min.

The absorption and desorption of toluene on ACF were studied in a continuous flow type system under dry and humid conditions and the results were compared with those on ACF after PDMS coating [45]. The system for the absorption and desorption experiment consists of gas mixture preparation part, reactor equipped with furnace and a GC. In the gas preparation part, constant flow of dry air containing ~86 ppm of toluene with and without water vapor was prepared and injected into the reactor consisting of linear SUS tube, in which ACF samples were packed. After passing through the reactor, the gas mixtures were analyzed by GC. For the absorption experiment, the samples packed in the linear SUS tube were outgassed at 300 °C for 1 h under dry air flow and after cooling down the sample temperature to 30 °C, absorption behaviors of toluene on the bare and PDMS-coated ACF were determined under dry and humid conditions, respectively. Please note that, in this work, the relative humidity under the humid condition was ~3 RH%, which was measured with a hygrometer. After the absorption experiment, the injection of toluene and water vapor was stopped and only a constant-flow of dry air was maintained for the removal of reversibly adsorbed species at 30 °C for 11 h. After that, the desorption behavior of toluene was analyzed with increasing the sample temperature from 30 to 300 °C with a ramping rate of 0.5 °C/min.

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