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Oxidation of Ethyl Ether on Borate Glass: Chemiluminescence, Mechanism, and Development of a Sensitive Gas Sensor

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A gas sensor was developed by using the chemiluminescence (CL) emission from the oxidation of ethyl ether by oxygen in the air on the surface of borate glass. Theoretical calculation, together with experimental investigation, revealed the main CL reactions: ethyl ether is first oxidized to acetaldehyde and then to acetic acid, during which main luminous intermediates such as $CH_3CO^{\bullet}$ are generated and emit light with a peak at 493 nm. At a reaction temperature of 245 °C, the overall maximal emission was found at around 460 nm, and the linear range of the CL intensity versus the concentration of ethyl ether was 0.12−51.7 μg mL^{-1} ($R = 0.999$, $n = 7$) with a limit of detection (3σ) of 0.04 μg mL^{-1}. Interference from foreign substances including alcohol (methanol, ethanol and isopropanol), acetone, ethyl acetate, *n*-hexane, cyclohexane, dichloromethane, or ether (*n*-butyl ether, tetrahydrofuran, propylene oxide, isopropyl ether and methyl tert-butyl ether) was not significant except a minimal signal from *n*-butyl ether (<2%). It is a simple, sensitive and selective gas sensor for the determination of trace ethyl ether.

Chemiluminescence generated on the surface of solid materials is an interesting phenomenon,[1,2] especially on a solid catalyst, for which the concept of cataluminescence (CTL) is established.[3] While the CTL phenomena of many molecules on a variety of catalytic solids have recently been reported, more efforts are still needed to exploit novel sensor materials with better selectivity and lower operation temperature.[4] On the other hand, many CL mechanisms are unclear and need to be further studied.

Generally, the whole CL reaction on solid is depicted as an adsorption−reaction−desorption mode.[3,5] Further, Nakagawa and Yamashita proposed that CL emission on solids involves recombinant radiation and radiation from excited species.[5] In the study of CL generation mechanisms, two strategies have frequently been used. One is to reason luminous intermediate species based on the similarity between the CTL spectra of the interested reaction and the known reaction,[6,7] and the other is based on the product analysis by GC or GC/MS.[8,9] For example, Lu et al.[10] have successfully utilized carboniogenesis theory to give a reasonable guess of the reaction route based on GC/MS assay. However, it is well-known that active reaction intermediates with very short lifetimes are difficult to identify, and this is the main reason why the study on CL reaction mechanisms has made slow progress in the past years.

Since the development of density functional theory[11−15] and the rapid increase in computer calculation capacity, high-precision quantum chemical calculations have been increasingly employed to study reaction processes. Theoretical calculation is capable of predicting many properties of molecules and reactions (especially reaction intermediates and transition states seldom studied experimentally), i.e., their structures and energy, thus luminous intermediate species could be relatively easily identified theoretically. Therefore, introducing theoretical calculation into the study of CL mechanisms can be a promising alternative or supplement.

Ethyl ether, one of the volatile organic compounds, is a common chemical extensively used in the industry and the laboratory. In addition to its pungent smell, its anesthetic effect, flammability and explosive nature pose a great risk to human health and safety. Therefore, it is a very important task to monitor its concentration in many cases. Many well-established methodologies for ethyl ether, such as GC and GC/MS, are excellent for in-laboratory measurement but not very well suitable for *in situ* determination. While semiconductor, piezoelectric and other types

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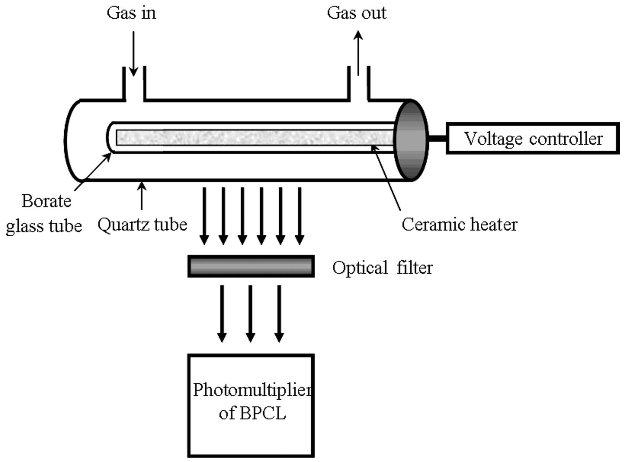

Figure 1. Schematic diagram of the ethyl ether gas sensor.

of sensors are greener alternatives,[16-20] there is still room for further development of simple, sensitive, selective and green analytical methods for ethyl ether.

Gas sensors based on CTL[21-27,10] not only provide direct, sensitive, selective and rapid analysis but also show a greener advantage attributed to the following factors: (i) no CL reagents or other reagents are needed for CL generation; (ii) exhausts after detection are usually of low toxicity and (iii) the apparatus can be simple and potentially portable for field analytical chemistry, thus avoiding sampling and potential pollution from the reagents used to preserve the samples.[28,29] In this work, therefore, a simple, sensitive, selective yet toxic reagent free gas sensor was developed by using the CL from the oxidation of ethyl ether on the surface of borate glass by air, and the CL reaction mechanism was studied by using theoretical calculation together with experimental investigation.

EXPERIMENTAL SECTION

Sensor Fabrication. As shown in Figure 1, the CL sensor consists of two main parts: a laboratory-made reaction cell coupled with a voltage controller and a commercial BPCL ultraweak luminescence analyzer (BP-II, Institute of Biophysics, Academia Sinica, Beijing, China) sensitive in the visible range. For this benchtop BPCL, neither the control unit (43 × 41 × 14 cm, and 6 kg) nor the detection unit (21 × 19 × 33 cm, and 8 kg) is bulky or heavy, and it can be easily miniaturized to a very compact one when necessary. The reaction cell was simply constructed by putting a cylindrical ceramic heater (i.d. = 5 mm) inserted into a borate glass tube (i.d. = 6 mm and length = 95 mm) in a quartz tube (i.d. = 11 mm and length = 95 mm). The temperature of the surface of the borate glass can be adjusted by controlling the voltage of the heater. A pump with an air cleaner provided a steady air flow stream at a controlled flow rate from 100 to 900 mL min^{-1}. Sample gas was delivered by the carrier stream and then reached the reaction cell for the CL detection with the BPCL analyzer. The data integration time for each signal point was 0.5 s, and a working voltage for the analyzer's photomultiplier tube was −800 V. The CL intensity was recorded with a computer and further processed with Microsoft Excel or OriginPro.

Instrumental Analysis for Mechanism Study. The mixture of N_2 and O_2 (v/v = 4:1) was employed as the carrier to avoid the interference caused by the impurity in the air. The resultant gases at 110 °C, 210 °C, and 245 °C from the sensor were collected in HPLC grade acetonitrile and then introduced into a Shimadzu QP2010 GC/MS system (Shimadzu Technologies, Japan) equipped with a Rtx-WAX column (30 m, 0.25 mm i.d., and 0.25 μm film thickness) for the analysis of the reaction products. The resultant gases at 160 °C were directly collected in a 3 L sampling bag (Hede Biotechnology Company, Dalian, China) and introduced into the same GC/MS system but with a Rtx-1MS column (30 m, 0.25 mm i.d., and 0.25 μm film thickness) and Nicolet 670 NEXUS FT-IR Spectrometer (Nicolet Company) for analysis. The resultant gases at 245 °C were also analyzed by FT-IR. The determination of acetaldehyde and acetic acid in the products (10 μL × 20 ethyl ether was oxidized and collected in 2 mL of deionized water) was carried out with an Agilent 6890 GC system (Agilent Technologies) equipped with an EC-WAX column (30 m, 0.53 mm i.d., and 1 μm thickness) and an FID detector. The CL emission spectrum was recorded with a Hitachi F-4500 fluorescence spectrometer (Hitachi Company, Japan) when the xenon lamp was turned off, with the emission slit width set at 20 nm.

Reagents and Materials. Borate glass tubes (using BJTY type glass from Beijing Glass Instrument Factory), soda-lime glass tubes and quartz tubes were fabricated by Chengdu Guoxiang Glass Instrument Factory (Chengdu, China), and ceramic heaters were purchased from Huanyu Electric Appliance Plant (Yixing, China). The borate glass was Pyrex type glass, and its main composition was almost the same as that of Pyrex 7740 as listed in Table S1 in the Supporting Information, in which another equally effective Pyrex type glass, GG-17, was also included. Except for the glass materials, no reagent was needed for the detection of ethyl ether in the air. Reagents used in this work were for the mechanism study, and they were of at least analytical grade. Standard ethyl ether (purity ≥ 99.5%) was purchased from Kelong Reagent Factory (Chengdu, China). Ar (99.99%), He (99.999%), N_2 (99.999%) and O_2 (>99.5%) were also tested as the carrier gas, respectively.

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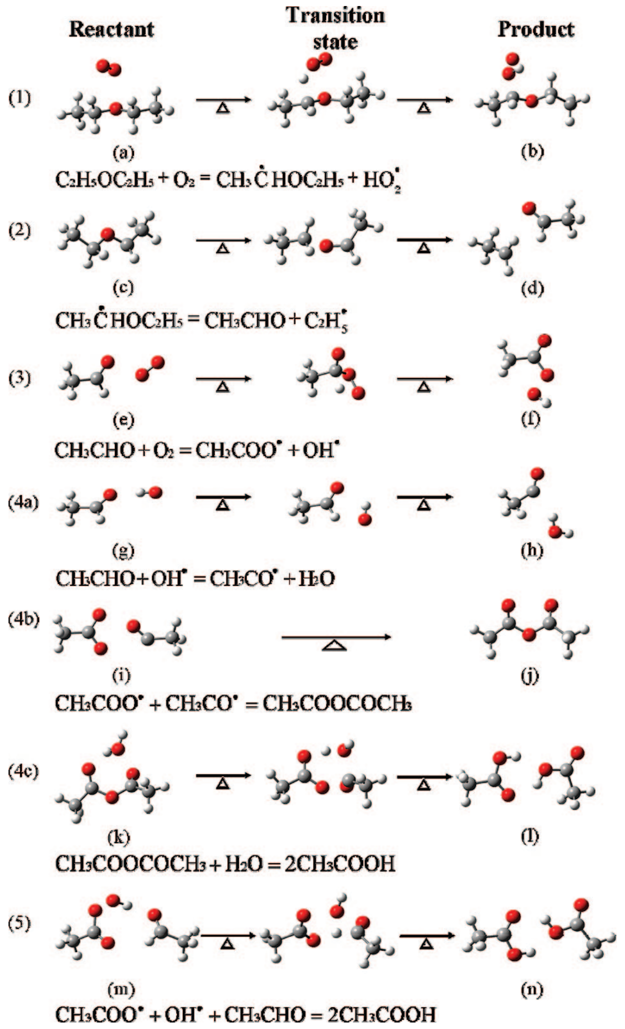

Figure 2. Possible reaction processes of the oxidation of ethyl ether by air with the CL emission. Large gray ball denotes C, small shaded ball denotes H, and large black ball denotes O.

RESULTS AND DISCUSSION

CL Generation Mechanism: Theoretical and Experimental Studies. (a) The Possible CL Reaction Processes. The results of GC/MS analysis showed that the oxidation of ethyl ether yields acetaldehyde, acetic acid, acetyl anhydride and other products (see Figure S1 in the Supporting Information). A similar reaction was first described by Isham and Vail[30] in as early as 1915 and later detailed by Lemay and Ouellet in 1955.[31] However, they did not observe the CL emission during its oxidation reaction since their work focused on the reaction and its products. In this work, we observed the CL emission and tried to clarify its generation mechanism of the oxidation reaction (see Figure 2), by using GC/MS data, theoretical calculation and relevant data in the literature.[30,31] The $\Delta_rH°$, $\Delta_rG°$ and ΔE_a of each corresponding reaction were calculated using the Gaussian 03 suite of programs (see the Supporting Information), and the results were listed in Table 1. It is suggested that the oxidation is a radical reaction in long chains, and the most probable initiation mode is the abstraction of α-hydrogen of ethyl ether by oxygen to form $CH_3\dot{C}HOC_2H_5$ (b).[31] The large radical then breaks into a molecule of acetaldehyde and a $C_2H_5^\bullet$ (d). The produced acetaldehyde is attacked by oxygen immediately, leading to two radicals: $CH_3COO^\bullet$ and $OH^\bullet$ (f). Thereafter, the reaction has two pathways to proceed to generate acetic acid: one is that acetaldehyde is attacked by $OH^\bullet$ with the generation of $CH_3CO^\bullet$ and water, and subsequently acetyl anhydride (formed by $CH_3COO^\bullet$ and $CH_3CO^\bullet$ collision) reacts with water (reactions 4a−4c); the other is that $CH_3COO^\bullet$ and $OH^\bullet$ react with acetaldehyde to yield acetic acid (reaction 5). As can be seen from Table 1, the ΔE_a of reactions 4a and 4c are much lower than that of reaction 5, and this means that reactions 4a−4c are favorable. This reaction pathway could well explain the phenomenon that acetic acid and acetyl anhydride were detected in the products at low reaction temperature [also see section (c)]. However, with increased temperature, reaction 5 is possible as well, and it provides a large amount of energy to excite luminous species.

Table 1. $\Delta_rH°$(298 and 518 K), ΔE_a and $\Delta_rG°$(298 and 518 K) of the Seven Possible Reactions

reaction	$\Delta_rH°$ (298 K) (kJ mol^{-1})	$\Delta_rH°$ (518 K) (kJ mol^{-1})	ΔE_a (kJ mol^{-1})	$\Delta_rG°$ (298 K) (kJ mol^{-1})	$\Delta_rG°$ (518 K) (kJ mol^{-1})
1	−44.9	−45.3	50.3	−36.7	−30.4
2	13.9	17.3	76.1	−13.4	−34.6
3	−280.7	−281.5	152.4	−267.2	−256.9
4a	−105.0	−103.5	8.3	−113.6	−120.5
4b	−326.2	−325.2		−269.6	−228.0
4c	−47.9	−50.5	97.3	−47.5	−46.3
5	−355.6	−356.3	187.5	−356.7	−357.2

(b) Prediction of the Main CL Intermediates. The CL spectra on borate glass were obtained with two spectrometers, as seen in Figure 3. These two CL spectra were similar, but the spectrum obtained with the fluorescence spectrometer showed higher spectral resolution, since only several optical filters instead of a monochromator were used in the BPCL luminescence analyzer for the CL detection. The CL spectrum with the fluorescence spectrometer shows about three main emission bands in the spectral region of 370−510 nm: 370−400 nm with peak at 376 nm; 450−470 nm with peak at 463 nm; and 480−505 nm with peak at 493 nm. The maxium CL was at 493 nm.

The calculated transition energies or their corresponding wavelengths of radiation from five possible CL intermediates, $CH_3\dot{C}HOC_2H_5$, $CH_3CO^\bullet$, CH_3CHO, CH_3COOH, and $CH_3COOCOCH_3$, from the first excited state to the ground state were 2.04 eV or 607 nm, 2.45 eV or 506 nm, 3.37 eV or 367 nm, 3.47 eV or 357 nm, and 3.36 eV or 369 nm, respectively. Considering the accepted error (10−20 nm, considering the transition energies, the spectral bandwidth of molecular absorption and the bandwidth of the spectrometers) between the theoretical value and the experimental one, the 370−400 nm emission band refers to the emission of acetaldehyde, acetic acid and acetyl anhydride; for the 480−505 nm band, $CH_3CO^\bullet$ is considered as one of the main CL intermediates. It is ascribed to the following: (i) compared with other reactions, the ΔE_a of reaction 4a is rather low, and this means that $CH_3CO^\bullet$ can be generated more rapidly; (ii) generally, reaction energy of over 168 kJ moL^{-1} is needed to afford the transition energies for CL emission in the visible range;[32] the released energy from the first four reactions is sufficient to afford

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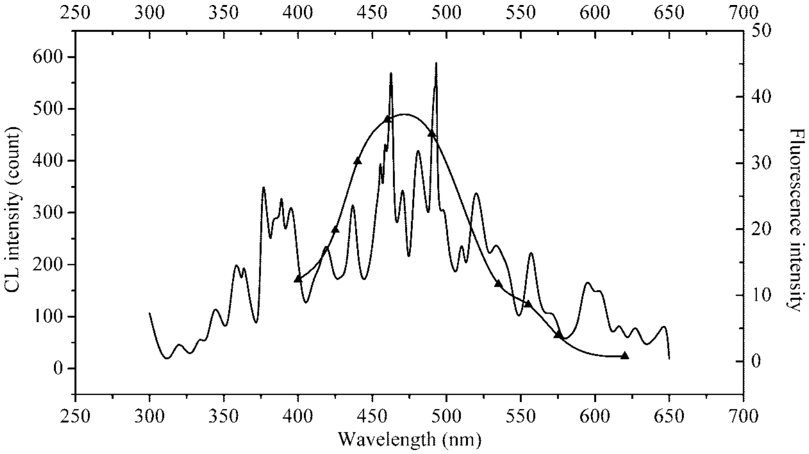

Figure 3. The CL spectrum on borate glass measured with the BPCL ultraweak luminescence analyzer and a Hitachi F-4500 fluorescence spectrometer. ▲ designates the spectrum measured with the BPCL using 9 optical filters, and the other trace is the spectrum measured with the Hitachi F-4500.

the transition energy of $CH_3CO^\bullet$; and (iii) the transition energy of $CH_3CO^\bullet$ (2.45 eV) can afford CL emission at 506 nm, which agrees well with the CL emission spectrum of higher spectral resolution in Figure 3. However, it still remains unknown which CL intermediates are responsible for the 450−470 nm emission band, and this calls for further improvement of the theoretical calculation.

(c) Effect of Reaction Temperature. Reaction temperature is a key parameter for the CL intensity. Although the Δ_rG° value of every reaction is negative, external heat is still needed to help reactants cross the energy barriers. At 148 °C, very weak CL started to appear when the concentration of ethyl ether was 97.7 μg mL^{-1} or higher; when the temperature was in the range of 148 to 210 °C, the CL reaction was not acute and the concentrations of the products were low. For example, at 194 °C, the amount of acetaldehyde was higher than that of acetic acid (see Figure S3 in the Supporting Information), indicating that at this temperature, energy was not sufficient for the rate-determining step of the oxidation of acetaldehyde to acetic acid (reaction 3 in Figure 2). Higher temperature (>210 °C) can afford sufficient energy and enhance the oxidation of acetaldehyde to acetic acid. The substantial increase of both the CL and the acetic acid concentration at the higher temperature strongly suggests some of main CL intermediates are generated during the oxidation process of acetaldehyde to acetic acid. (See Figures S3 and S4 in the Supporting Information.) The CL intensity increased with temperature when higher than 210 °C (see Figure S4 in the Supporting Information). However, signal-to-noise ratio reached a maximum at around 245 °C, and then decreased at higher temperature mainly due to the increasing noise caused by heat irradiation. Therefore, 245 °C was selected for use in this work.

Two points should be mentioned here. First, Isham and Vail[30] reported the oxidation could begin at a temperature as low as 110 °C, but no CL was observed in the flow-through detection system and no products were detected in this work (see Figure S1(b) in the Supporting Information). In a closed detection mode, however, relatively low but lasting CL emission was observed with an injection of 0.1 mL of ethyl ether. This indicates that the whole reaction was not acute at the low temperature, and the reaction was slowed by the loss of heat and the short reaction time caused by the flowing carrier stream. Therefore, higher temperature is needed in the flow-through mode in this work. Second, at 160 °C (self-combustion point of ethyl ether), combustion products such as CO_2 were not found, but at 245 °C we did detect CO_2 (see Figure S2 in the Supporting Information). On the other hand, acetaldehyde, acetic acid, methanol, ethanol and acetyl anhydride were all found in the products collected at 160 °C, 210 or 245 °C (see Figure S1 in the Supporting Information). According to Salooja,[33] when the temperature is lower than about 490 °C, the oxidation of ethyl ether is in the "cold flame" state, and bright flame is not observed; under the "cold flame" condition, the oxidation products contain not only CO_2 but also many organic compounds such as acetaldehyde, acetic acid, methanol, and ethanol.

(d) Effect of Carrier Gas. As discussed earlier in this article, the proposed mechanism shows the key role of oxygen, that is, the reaction is initiated from the abstraction of α-hydrogen of ethyl ether by oxygen, and the attack to acetaldehyde again by oxygen leads to the formation of the main CL intermediate ($CH_3CO^\bullet$). To further confirm this reaction route, other non-oxidative gases including nitrogen, helium or argon were also used to replace air, but no significant CL signal was observed (see Figure 4) compared to the case of air, thus further proving the above statement. Further investigation showed that the CL intensity increased impressively with the concentration of O_2, and it was steady when the concentration of O_2 was ⩾80%. Air is, however, ultimately selected as the carrier gas for practical consideration.

The effect of the carrier (air) flow rate on the CL intensity was investigated in the flow rate range of 100−900 mL min^{-1} at the heating voltage of 125 V. It can be seen from Figure S5 in the Supporting Information that both signal intensity and signal-to-noise ratio reached maximum at 500 mL min^{-1}. The oxidation process is under a diffusion-controlled condition at lower flow rate (<500 mL min^{-1}), that is, adsorbates (ethyl ether molecules) on the surface of borate glass react rapidly as soon as they are transported to the surface; thus the higher the flow rate, the stronger the CL under this condition. The air flow rates higher than 500 mL min^{-1} lead to insufficient contact/reaction time, thus decreasing the CL. Therefore, 500 mL min^{-1} was chosen for use in this work.

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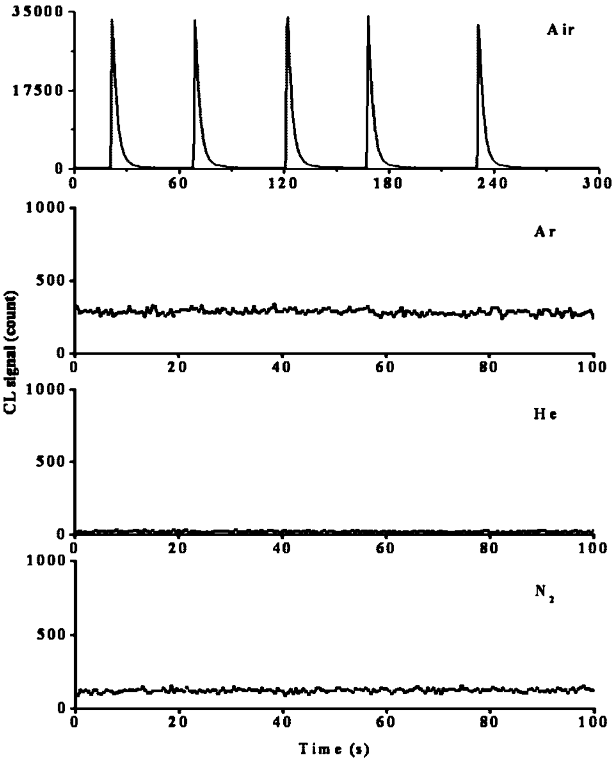

Figure 4. The effect of different carrier gas on the reaction. Temperature, 240 °C; flow rate, 500 mL min^{-1}; ethyl ether concentration, 23.8 μg mL^{-1}; and surface material for the reaction, borate glass.

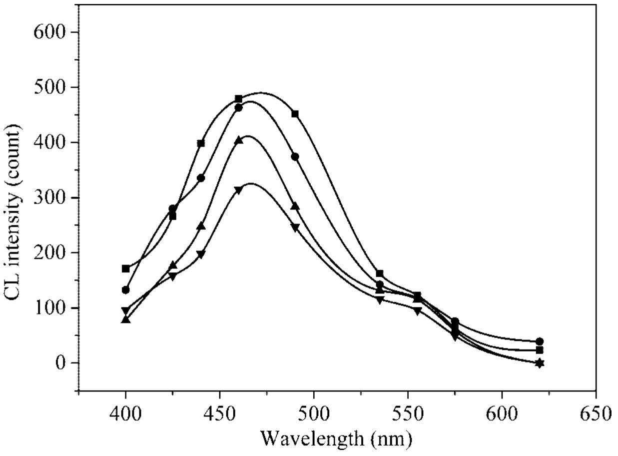

Figure 5. The CL spectra on four surface materials (■ borate glass, ● ceramic, ▲ quartz, and ▼ soda-lime glass) measured by luminometer. Temperature, 245 °C; carrier flow rate, 500 mL min^{-1}; and ethyl ether concentration, 23.8 μg mL^{-1}. Note the CL intensity is attenuated by the optical filters.

Effect of Surface Material. Further study showed that surface material could affect the CL intensity (sensitivity), and it played a vital role in the selectivity of the present sensor. As can be seen from Figure 5, among the four surface materials, the CL signal intensity on borate glass was the highest. It is worthwhile to note that the CL spectra on these surface materials were similar, with the same maximal CL emission at about 460 nm, indicating similar or same CL generation routes on each of the four surface materials. The main component in the glass is silicon dioxide which has low or no catalytic effects, while borate glass also contains 11.9% boric oxide, which is known as one of the electron-deficient compounds and may easily accept lone pair electrons of oxygen from ethyl ether. Thus, compared with quartz glass and soda-lime glass, it may absorb more ethyl ether molecules for oxidation, thus stronger CL emission. In order to further support the above explanation, one-third of a soda-lime glass tube's surface was sintered with boric oxide, and it was found that the CL intensity even surpassed that on borate glass (see Figure S6 in the Supporting Information).

On borate glass, interferences from foreign substances such as alcohol (methanol, ethanol and isopropanol), acetone, ethyl acetate, *n*-hexane, cyclohexane, dichloromethane, and ether (*n*-butyl ether, tetrahydrofuran, propylene oxide, isopropyl ether and methyl tert-butyl ether) were not detectable except very low signal level (<2%) from *n*-butyl ether (see Figure S7 in the Supporting Information). Similar selectivity was obtained on quartz glass or soda-lime glass, but the CL intensity was higher on borate glass. However, when the solid material was replaced with ceramic, acetone, isopropanol and *n*-hexane also generated weak CL. Ceramic used in this work contains some alumina and other substances as catalysts for the generation of the CL from acetone, isopropanol and *n*-hexane, similar as reported by Zhang et al.[34] The active components in ceramic may help the oxidation of ethyl ether as well, thus the CL intensity on ceramic was comparable with that on the borate glass. Finally, borate glass was selected as the optimal surface material in this work due to its good sensitivity and selectivity for ethyl ether.

Analytical Figures of Merit. Under the optimal experimental conditions (air flow rate, 500 mL min^{-1}; reaction temperature, 245 °C; 460 nm for the CL detection; and borate glass as the surface material), the linear dynamic range of the CL intensity versus ethyl ether concentration was 0.12−51.7 μg mL^{-1}, with a limit of detection (3σ) of 0.04 μg mL^{-1}, 30-fold lower than the permissible exposure limit for ethyl ether of 1.2 μg mL^{-1} as an 8 h time-weighted average concentration according to the Occupational Safety and Health Administration. The linear regression equation is described by $y = 29.4x + 18.9$ ($r = 0.999$, and $n = 7$), where y is the relative CL intensity, x is the concentration of ethyl ether, and r is the linear correlation coefficient. Relative standard deviations ($n = 5$) were 0.8%, 1.7% and 1.9% for 1.55, 15.5 and 41.4 μg mL^{-1} ethyl ether, respectively.

CONCLUSION

In this work, the CL from the oxidation of ethyl ether by air on borate glass surface was discovered. It is demonstrated that the introduction of theoretical calculation into the study of CL generation mechanism is helpful in the clarification of the main route for the CL emission and in the prediction of the main CL intermediates such as $CH_3CO^{\bullet}$. Further, the key roles of oxygen and reaction temperature can be well explained by the proposed mechanism. The proposed ethyl ether gas sensor offers the following distinct advantages: (i) compared with GC and GC/MS, it is a simple and cost-effective sensor; (ii) it is a greener sensor, since no toxic reagent/solvent is needed, and the exhaust is of low toxicity and at low concentra-

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tions; and (iii) it shows much better sensitivity and selectivity, and faster response (less than 30 s) than many common VOC sensors. Thus, it should have a promising future in on-site monitoring of ethyl ether in air in factories, storehouses, forensic analysis and more.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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