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Identification and determination of formaldehyde, benzene and ammonia in air based on cross sensitivity of cataluminescence on single catalyst

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ABSTRACT

A cataluminescence (CTL) based method for simultaneously identifying and determining formaldehyde (HCHO), benzene (C_6H_6) and ammonia (NH_3) in air was proposed. CTL is emitted from the surface of nano-sized $Ti_2YAl_3O_{10}$ contained in a CTL reactor. Three analysis wavelengths of 350 nm, 440 nm and 560 nm were selected. The surface temperature of sensing materials was 340 °C. The flow rate of air carrier was 140 mL/min. The limits of detection were 0.07 mg/m^3 for HCHO, 0.10 mg/m^3 for C_6H_6 and 0.15 mg/m^3 for NH_3. The linear ranges of CTL intensity versus analyte concentration were 0.2–66.4 mg/m^3 for HCHO, 0.5–71.5 mg/m^3 for C_6H_6 and 0.5–63.8 mg/m^3 for NH_3. The recoveries of 10 testing standard samples was 97.5%–103.1% for HCHO and 96.8%–102.8% for C_6H_6 and 98.1%–103.7% for NH_3. Common coexistence matters, such as acetaldehyde, toluene, ethyl benzene, methylamine, ethylamine, methanol, ethanol, sulfur dioxide, hydrogen sulfide and carbon dioxide, did not disturb the determination. The relative deviation of CTL intensities was less than 3% for continuous 200 h detection, which demonstrated the longevity and steady performance of nano- $Ti_2YAl_3O_{10}$ to HCHO, C_6H_6 and NH_3.

1. Introduction

Formaldehyde, benzene and ammonia are three of the most common indoor air pollutants [1,2]. Formaldehyde can be released from many house products which were made from pressed wood panels [3]. The main sources of benzene in air are exhaust gas of motor vehicles, the use of paints and glues, the combustion of wood, the fermentation of organic wastes, and smoking of cigarette [4]. Ammonia in indoor air is considered to release mainly due to hydrolysis of urea which may be present in antifreeze additives of concrete buildings in wintertime [5].

People spend much of their time indoors where they are continuously exposed to low concentrations of a wide variety of air pollutants. Formaldehyde can cause indisposition of throats, irritation of eyes and noses, difficult breathing, injury of respiratory organs, and even asphyxia [6]. Benzene can induce oxidative stress which may affect insulin resistance (IR). As a physiological condition comprising an inadequate response to insulin, IR plays a key role in the pathogenic pathways involved in metabolic syndrome, diabetes mellitus (DM), cardiovascular disease, and obesity [7]. Ammonia can strongly stimulate the respiratory tract, eye and skin. Prolonged exposure to ammonia, even if low concentration, can cause serious health effects, such as rhinitis, nasopharyngitis, pharyngitis, tracheitis, bronchitis and other inflammation of different types and levels [8].

Various methods were applied to determine formaldehyde, benzene or ammonia. Such as flow injection analysis [9,10], chemiluminescence [11], photo electrochemistry [12,13], gas chromatography [14,15], ion chromatography [16], liquid chromatography [17], fluorescence [18] and so on. In situ or online methods were becoming increasingly important [19–22]. There is no report on the simultaneous determination of formaldehyde, benzene and ammonia or their cross interference in the literature.

Cataluminescence (CTL) is an emission of electromagnetic radiation produced by catalytic oxidation reactions that yield excited intermediates which can emit rays on falling to the ground state on the surface of catalyst [6,23]. CTL spectra from different reaction are different, so they can be taken as the basis of analysis. Now, CTL has been considered as a promising energy transduction mechanism for

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fabricating gas sensor because of its outstanding advantages such as long life, easy miniaturization, fast response, needless luminescent reagent, and etc. In recent years, a series of CTL analytical applications have been attempted to develop for a variety of gaseous molecules by either exclusive sensor or sensor array [24–34].

Utilizing more information in the CTL spectral profile is favorable to monitor multi- component gas. So, we tried to study the sensitive behavior of a variety of components on a catalyst which is better economy than multiple gas sensors array and easier to implement than different working temperature, and established several methods for the simultaneous determination of two components [35–37].

In this work, we try to screen a proper catalyst and express the cross sensitive properties of CTL from three components on it, and establish an on-line method for simultaneously determining formaldehyde, benzene and ammonia.

2. Experimental

2.1. Chemical reagents and materials

All reagents used were of analytical grade without further purification. Tetrabutyl titanate, methanol, ethyl acetate, aluminum nitrate, yttrium acetate, hydrochloric acid and citric acid were purchased from Beijing Chemical Regent Co., LTD. (Beijing, China). Various standard gases of formaldehyde, benzene, ammonia, acetaldehyde, toluene, ethylbenzene, methylamine, ethylamine, methanol, ethanol, sulfur dioxide, hydrogen sulfide, carbon dioxide and their mixture in artificial air were purchased from Beijing Ya-nan Gas Co., LTD. (Beijing, China). Distilled water was used throughout the whole experiment.

2.2. Preparation of sensing materials

In order to probe into the efficiencies of different sensing materials in the catalytic oxidation of formaldehyde, benzene and ammonia, a great deal of nanosized materials were prepared. The procedure for synthesis of nano- $Ti_2YAl_3O_{10}$ by means of a sol-gel method was as follows: tetrabutyl titanate was dissolved in methanol at room temperature, then 1:1 (v/v) ethyl acetate and distilled water were slowly added into the solution, and Ti sol was formed by continuously stirring the solution more than 10 h. At the same time, aluminum nitrate and yttrium acetate were dissolved in hydrochloric acid solution and then citric acid was added into the solution. The mix solution was added into Ti sol above, and Ti-Y-Al gel was formed after stirring for 3 h at room temperature. The atom ratio of Ti:Y:Al was 2:1:3. This gel was subjected to aging for 5 h at room temperature, drying for 2 h at 105 °C, cooling to room temperature, rubbing, and roasting for 4 h at 400 °C, successively, to finally get nano- $Ti_2YAl_3O_{10}$. The TEM photograph in Fig. 1 shows that the average granular size was about 30 nm.

2.3. Apparatus of cataluminescence

The self-designed tri-wavelength CTL system used in this work is shown in Fig. 2.

The system, an improvement from references [6,35–37], mainly includes four parts. They are (1) CTL reactor (a cylindrical ceramic heater of 5 mm in diameter sintered a thickness of 0.08–0.15 mm sensing materials was placed in the middle of a quartz tube of 10 mm in diameter possessing gas entrance-exit), (2) temperature controller (the surface temperature of ceramic heater can be adjusted from room temperature to 550 °C), (3) optical filter (transitable rays can be selected from 400 nm to 745 nm), and (4) weak luminescence analyzer (CTL singles can be processed by photo multiplier, photons counter and computer).

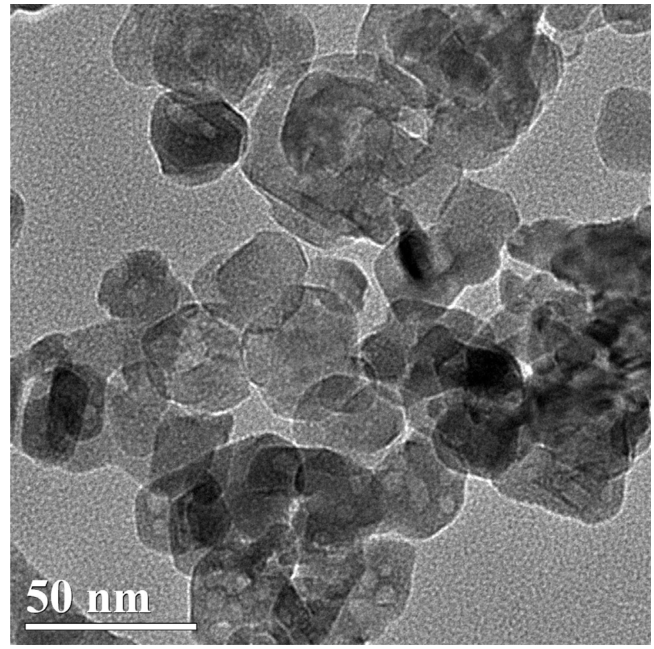

Fig. 1. TEM photo of nano- $Ti_2YAl_3O_{10}$.

2.4. Experimental procedures

The gaseous samples are directly introduced through CTL reactor through entrance by air as carrier. Formaldehyde, benzene and ammonia in air are selectively oxidized on the surface of sensitive materials at a certain temperature. The luminescence intensities passing through three optical filters are respectively recorded by a BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). Each CTL signal is a difference value of sample signal and background signal. At the beginning of experiment, every sensitive material is heated at roasting temperature for 30 min in pure air to avoid the influence of previous adsorbates.

3. Results and discussion

3.1. Choice of sensing materials

The heterogeneous catalytic reaction was carried out on the surface of the solid catalyst. Firstly, the reactant molecules must be chemically adsorbed on the surface of the catalyst. Secondly, the adsorbed reactant molecules can react with adsorbed oxygen in the appropriate conditions. Finally, the reaction product can be removed from the surface of the catalyst. When a variety of molecules reach the surface of the catalyst, there is often a competitive adsorption and reaction. If a molecule is easy to be adsorbed on the catalyst, and the reaction with the adsorbed oxygen is faster than other one, and the reaction product is easy to be removed, so it has a competitive advantage on the catalyst.

The catalytic properties of metal oxides have been widely concerned. Although the CTLs of formaldehyde, benzene, ammonia, acetaldehyde, toluene, ethylbenzene methylamine and ethylamine can be observed on all of TiO_2, SnO_2, ZnO and Al_2O_3, luminous intensities of formaldehyde benzene and ammonia are stronger from TiO_2 than from other metal oxides. At the same time, formaldehyde has an evidently competitive advantage at 340 nm and benzene at 610 nm. Further studies found that composite TiO_2