



Decontamination of chlorine gas by organic amine modified copper-exchanged zeolite



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ABSTRACT

Removal of chlorine gas (Cl_2) from air is of critical requirement in order to address point-source emissions possibly during a terrorist attack or an industrial accident resulting in Cl_2 contamination of the atmosphere. In this work, copper (Cu) exchanged zeolite Y (CuY) was functionalised with triethylenediamine (TEDA) and the capacity to remove Cl_2 was evaluated. The materials were characterised by nitrogen (N_2) adsorption–desorption studies, Fourier Transform Infrared (FTIR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS). The materials' ability to remove Cl_2 was investigated via a dynamic breakthrough test. Copper exchanged zeolite displayed a low adsorption of Cl_2 in spite of its large surface area. However, Cl_2 removal greatly improved following functionalisation with TEDA. XPS analysis revealed that Cl_2 was removed via a catalytic hydrolysis reaction where adsorbed water vapour transformed Cl_2 into Cl^- which could be further trapped in the zeolite structural framework. Moisture could increase the Cl_2 removal capacity, but the competition for adsorption between water and chlorine molecules was also observed. The spent adsorbent after exposure to Cl_2 could be easily recycled with an excessive water vapour treatment. The reusability was also investigated and the adsorbent could be used for more than five times. This material can potentially be used in air filters. It may provide an efficient way for decontaminating Cl_2 during a terrorist attack or an industrial accident.

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1. Introduction

Chlorine gas (Cl_2) has a broad range of application in a variety of industries. It is commonly used as a bleaching reagent by textile manufacturers [1]. It is also an important reagent in the pharmaceutical, plastic and agrochemical industries [2]. Moreover, it is used as a disinfectant in water treatment. However, Cl_2 is also one of the chemical warfare agents, which was used in World War I. An exposure to 20 ppm of Cl_2 up to 1 h can lead to a life-threatening effect for nearly all individuals [3]. Therefore, developing a highly

efficient and commercially feasible material for the removal of Cl_2 from air is very important in order to address point-source emissions possibly during a terrorist attack or an industrial accident causing significantly excess Cl_2 concentration in the atmosphere.

The removal of gas-phase chlorine by adsorption has not been widely reported in the open literature. Activated carbon impregnated with metal salts, such as copper chromate plus triethylenediamine (TEDA) is commonly used for chlorine removal [4,5]. However, carbon based adsorbent may potentially possess some inherent drawbacks for Cl_2 removal. For example, in graphene material, carbon can bind chlorine atom through transferring charge to adsorbed chlorine atom, but chlorine can migrate on the surface of carbon particle without an energy barrier, and due to the strong Cl–Cl interaction the Cl_2 molecules are formed resulting in a faster desorption [6]. This indicates that the adsorption of Cl_2 on carbon material is a reversible process. It was also reported that addition of copper chromate or copper chromate plus TEDA on carbon adsorbent decreased the breakthrough time by decreasing the micropore volume [7].

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Recently zirconium hydroxide impregnated with TEDA was developed as a new chlorine adsorbent [8]. It was reported that removal of Cl_2 was greatly improved by the TEDA impregnation where TEDA acted as a catalyst, promoted the hydrolysis of Cl_2 gas into hydrogen chloride (HCl) [8]. However, similar to carbon materials [9,10], amorphous nature of the material network resulted in the lack of control over the impregnant's distribution, and thus lacked stable interaction between the impregnant and the substrate, which possibly could result in a secondary contamination.

Zeolite material possesses a large cationic exchange capacity, relatively large surface area and unique micropores [11]. Consequently, the surface of zeolite can be easily functionalised with specific functional groups by either ion exchange or electrostatic attraction [12]. A well-defined crystal structure together with a large volume of micropores might qualify zeolite as an excellent but inexpensive catalyst support for Cl_2 decontamination and avoid the disadvantages which occur in carbon based materials. In this work, we developed a copper (Cu) exchanged plus TEDA modified zeolite for Cl_2 adsorption. The amine molecule could be chemically supported to the exchanged metal ions on the zeolite surface to provide well-defined and tailored active sites. The performances of modified zeolite were evaluated by dynamic breakthrough test for Cl_2 adsorption. The mechanism for Cl_2 removal was also explored along with the possibility of adsorbent recycling for repeated use.

2. Experimental section

2.1. Adsorbent preparation

The Cu-exchanged zeolite Y (CuY; Si/Al = 3.4) was prepared by using CuCl_2 as the precursor. First, ammonium exchanged zeolite (NH_4Y) (10 g) was added to 50 mL of 0.5 M CuCl_2 solution. The resultant solution was sealed in a Pyrex bottle and kept at 105 °C for 3 h. The powder was collected by filtration and then washed with copious amount of deionised water. After being dried at 60 °C overnight, the powder was calcined at 500 °C for 4 h.

Triethylenediamine (TEDA) was loaded on the CuY zeolite by sublimation method. Typically, 1 g of CuY powder was mixed with the desired quantity of TEDA and sealed into a 100 mL Pyrex bottle. The Pyrex bottle was kept in an oven at 80 °C for 24 h in order to adsorb the TEDA on the exchanged copper sites. The samples were referred to as CuY-*x*TEDA, where *x* is the weight percent of TEDA loading.

2.2. Cl_2 dynamic breakthrough test

A micro-scale breakthrough apparatus was developed to assess the Cl_2 adsorption behaviour of samples. The breakthrough dynamic test was operated at room temperature and atmospheric pressure. The gas streams were 1518 ppm Cl_2 (4410 mg m^{-3}) prepared by diluting 4% Cl_2 in N_2 with dry air or with 27% moist air. The flow of 4% Cl_2 was controlled by a mass flow meter. The flow rate of air was monitored by a rotameter. The two flow meters were calibrated with a bubble meter. The total flow rate of inlet gas was fixed at 115 mL min^{-1} . About 1 mL of sample was packed into a 1.0 cm inner-diameter glass column. The Cl_2 concentration in the outlet gas was measured using a Dräger XAM7000 system equipped with an electrochemical sensor for Cl_2 . The flow of Cl_2 was arbitrarily stopped when the breakthrough concentration was 10 ppm, following which desorption process was studied by purging the sample with air only. The adsorption capacity of each adsorbent was calculated by integrating the area above the breakthrough curve by taking the Cl_2 concentration in the inlet gas, flow rate, breakthrough time and amount of chlorine desorbed into consideration. All Cl_2 adsorption tests were replicated thrice.

2.3. Materials characterisation

Surface area analysis was based on the BET (Brunauer, Emmett and Teller) N_2 adsorption/desorption method by using a Gemini 2380 automated gas adsorption analyser. Samples were degassed at 110 °C for a minimum of 12 h.

Fourier Transform Infrared (FT-IR) spectroscopy was conducted by using a Cary 600 series FTIR spectrometer (Agilent Technologies). Samples were characterised in the form of a KBr disc that was prepared by mixing the sample with KBr at a ratio of 1% (w/w), grinding into a fine powder, and compressing into discs.

X-ray Photoelectron Spectroscopy (XPS) data were obtained on a Kratos Axis ULTRA X-ray photoelectron spectrometer. The incident radiation was monochromatic aluminium (Al) X-rays (1486.6 eV) at 150 W (15 kV, 15 ma). The carbon (C) 1s peak at 284.5 eV was used as a reference for the calibration of binding energy scale.

3. Results and discussion

3.1. Characterisation of materials

The BET surface areas and textural structures of CuY and modified adsorbents were determined by N_2 adsorption–desorption isotherms. As shown in Table 1, Cu-exchanged zeolite Y (CuY) exhibited a large BET surface area (528 $\text{m}^2 \text{g}^{-1}$), among which 471 $\text{m}^2 \text{g}^{-1}$ is mainly contributed by microporous channels among zeolite crystallites [13]. The external surface area of zeolite crystallites was measured to be 57 $\text{m}^2 \text{g}^{-1}$. When the zeolite surface was modified with TEDA, the microporous surface area decreased dramatically, while the external surface area only decreased slightly. For example, at 10% TEDA loading, the micropore surface area significantly decreased from 471 $\text{m}^2 \text{g}^{-1}$ to 80 $\text{m}^2 \text{g}^{-1}$ and the external surface area decreased from 57 $\text{m}^2 \text{g}^{-1}$ to 35 $\text{m}^2 \text{g}^{-1}$. This indicated that the modification of CuY crystallites with organic molecules resulted in blockages of the microporous channels [14]. At 15% TEDA loading, the outer surface of zeolite crystallites should have been fully covered by organic molecules, since the microporous surface area almost completely disappeared.

The structural changes of CuY before and after TEDA modification were investigated by FTIR spectroscopy (Fig. 1). The major changes could be observed in the wavenumber range between 1200 cm^{-1} and 1600 cm^{-1} . For pristine TEDA molecules the band at 1316 cm^{-1} could be assigned to C–H wagging modes and the band at 1458 cm^{-1} was attributed to C–H scissoring vibrations [15]. For CuY–10%TEDA, these two bands were found at 1324 cm^{-1} and 1470 cm^{-1} , respectively. According to a previous study, the shift to higher frequency for these bands normally indicated the formation of TEDA salt when TEDA molecule reacted with a cation [16]. In this study, on the substrate of Cu^{2+} exchanged zeolite Y, these bands shifts could be attributed to the strong interaction between the Cu^{2+} exchanged zeolite Y and TEDA molecules.

The coordination between Cu^{2+} and TEDA in CuY–TEDA samples was also supported by their N 1s photoelectron spectra (Fig. 2). Cu^{2+} –TEDA complex prepared by titrating TEDA with Cu^{2+} followed by drying at 60 °C was used as the reference and compared with CuY–TEDA samples. As shown in Fig. 2, the N (1s) photoelectron spectra consisted of two N species. The low-energy peak at 400 eV could be assigned to the bare nitrogen atom [17]. The peak at 402 eV was observed when nitrogen atom associated with the cation, such as Cu^{2+} and H^+ [8]. In this study, NH_4Y was used as the starting material which was first replaced with Cu^{2+} and then calcined at 500 °C. As the XPS spectra of CuY–10%TEDA was consistent with that of the reference sample, i.e., Cu–TEDA complex, exhibiting the presence of two atomic nitrogens, it could be

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