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Metal organic frameworks for gas-phase VOCs removal in a NTP-catalytic reactor

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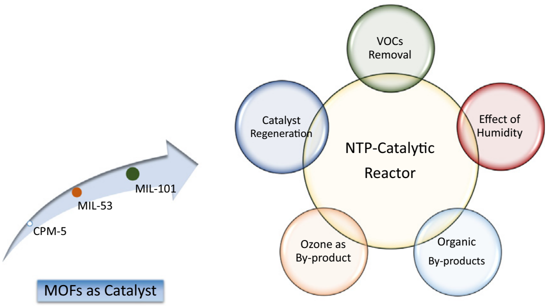
HIGHLIGHTS

- MIL-101, MIL-53 and CPM-5 were used for VOCs removal in a NTP-catalytic reactor.
- High isobutanol and toluene removal efficiency were obtained over all catalysts in dry air.
- MIL-53 showed the best adsorption capacity in humid air.
- MIL-101 and MIL-53 demonstrated almost the same oxidation performance.
- FTIR spectroscopy of fresh and regenerated catalysts showed no significant structural change.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, three different metal organic frameworks, MIL-101, MIL-53, and CPM-5, are used as dual functional adsorbent/catalysts in a non-thermal plasma (NTP)-catalytic reactor. The adsorption and oxidation evaluations of these MOFs for the removal of one (1) ppm toluene and isobutanol are performed at both dry (RH = 0%) and humid (RH = 30%) conditions. Results show that at dry air condition, MIL-101 possesses the highest adsorption capacity; however, at 30% RH, MIL-53 capacity surpasses MIL-101 and CPM-5. The results of NTP-catalytic oxidation reactions demonstrate a high removal efficiency of isobutanol (100%) and toluene (~90%) for all three MOFs at dry air condition. At 30% humidity, on the other hand, the catalysts removal performance decreases. During the NTP-oxidation reaction different organic compounds and ozone are detected as by-products. Finally, FTIR spectroscopy of fresh and regenerated catalysts (MIL-101, MIL-53 and CPM-5) does not show a significant structural change.

1. Introduction

Development of non-thermal plasma (NTP) technology and its remarkable capacity for VOCs destruction has opened a new field of study in the area of air treatment [1,2]. In a NTP process, applying a high electrical voltage results in the formation of reactive species, ions and radicals due to the collision of highly energetic electrons with molecules in the air [3]. As a result, destruction of

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Abbreviations: AC, Alternative Current; BET, Brunauer-Emmett-Teller; CPM-5, Crystalline porous material; DBD, Dielectric barrier discharge; DFA/C, Dual functional adsorbent/catalyst; FTIR, Fourier transform infrared; HV-AC, High voltage-alternative current; MIL-101, Materials of Institute Lavoisier-101; MIL-53, Materials of Institute Lavoisier-53; MOF, Metal organic framework; NTP, Non-thermal plasma; RH, Relative humidity; VOC, Volatile organic compound.

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pollutants including VOCs happens at ambient temperature [4]. However, incomplete oxidation and formation of harmful by-products such as O_3, CO, NO_x and other VOCs are the main disadvantages of this technology [3,5,6]. Furthermore, due to a high level of energy consumption, utilizing NTP technology is not cost effective, especially when this technique is considered for the abatement of low concentration levels of VOCs in indoor environment [3,5]. As a solution, utilizing a catalyst in NTP reactor is proposed [5,7].

Implementation of catalyst in a NTP reactor enhances VOCs removal efficiency and CO_2 selectivity and decreases the by-products formation due to the synergic effect of plasma and catalyst [8]. Despite a reduction in the demand of electricity in such a system, energy efficiency is still a concern when the concentration of pollutants is very low. In such conditions, utilizing an adsorbent for pre-concentrating pollutants becomes attractive due to lower energy consumption [9]. Therefore, as a new approach, reactive adsorption process was developed [10–13]. This method specifically attracted the interests of researchers for economizing energy consumption in the plasma catalyst field [14–17]. In this method, the VOC removal performance is a function of both the adsorption characteristics and oxidation ability of the media, which is used as the adsorbent/catalyst [18]. Therefore, selecting an appropriate dual functional adsorbent/catalyst (DFA/C) is a crucial aspect if this method is considered for indoor air treatment.

In addition to oxidation capability, an employed DFA/C should possess high adsorption capacity and hydrophobicity especially at low concentration levels of VOCs and in the presence of humidity. The higher the capacity of the media for VOCs storage, the greater the amount of pollutants that can be adsorbed on its surface. As a result, energy consumption is decreased during a reactive adsorption process. Several studies have been conducted on NTP-catalyst in the presence of different types of DFA/Cs, including metals $^{and}/_{or}$ metal oxides, which are used as a support for porous materials such as activated carbon and zeolites [16,17,19–21]. Due to their excellent characteristics, zeolite based media show high removal efficiency for most VOCs. However, the relatively small pore sizes of these materials limit the application of zeolites for removal of large VOCs [22].

Metal organic frameworks (MOFs) as a new class of porous materials exhibit excellent specifications, such as exceptionally large surface area, high gas adsorption, substantial storage capacity, and extra-high porosity [23–26]. The uniform crystal size and size distribution of MOFs [27,28] facilitate mass transport phenomena, including adsorption of target compounds, diffusion into pores, and desorption of the products, provide a favorable condition for catalyzing a reaction [29–31]. MOFs also have an abundant amount of metal content (~20–40 wt%) in the form of metal nods, with free and exchangeable active sites [27]. The presence of these metal sites induces heterogeneous catalytic properties in MOFs [32]. The above-mentioned specifications of MOFs suggest that these materials can be excellent candidates as DFA/Cs for the removal of VOCs in a NTP-catalytic reactor. However, the potential performance of these materials for the degradation of VOCs has not been investigated yet in plasma catalytic processes.

Accordingly, in this study three different MOFs – MIL-101 (MIL: Materials of Institute Lavoisier), MIL-53, and CPM-5 (CPM: Crystalline Porous Material) – are used as catalysts in a NTP-catalytic system. All of these MOFs have been previously synthesized, characterized, and their VOCs adsorption behaviors have been investigated in dry air and in the presence of humidity [33]. These MOFs have been selected due to their thermal and chemical stability, which is explained before [33]. In the current study, the removal efficiency of these MOFs for the degradation of one (1) ppm of toluene and isobutanol in dry air and at 30% relative humidity (RH) is explored. In addition, formation of organic by-products and ozone is studied. Finally, the structural characteristics of utilized catalysts before and after NTP-catalytic reactions are studied.

2. Experimental

2.1. Experimental set-up and measurement apparatus

VOC removal efficiency of the selected MOFs was evaluated at a total flow rate of 1 $L.min^{-1}$ and ambient temperature (21 ± 1 °C). The experimental set-up is illustrated in Fig. 1.

In this dynamic system, dry air was supplied from a compressed air reservoir (A) and passed through a regulator (B) to adjust the pressure. A water bubbler (D) was utilized upstream to provide the required humidity. The amount of the humidity was adjusted via a control valve (C) and the airflow rate was controlled by means of mass flow controllers (Matheson, Model 8274) (E). A syringe pump (KD Scientific, Model KDS-210) injected the target VOC at the desired rate into the system (F). Afterward, the air stream containing the target VOC passed through the catalyst in the reactor (G). The upstream and downstream samples were collected from the reactor in stainless steel adsorption sampling tubes (Supelco Air Toxics, packed with Tenax-TA 49) (H) by means of sampling pumps (17G9 GilAir-3 Sampler) (I) in an adjusted flow rate of 50 $mLmin^{-1}$ for a period of 20 min. These samples were analyzed using a gas chromatography/mass spectroscopy (GC/MS, Perkin Elmer, Clarus 500) coupled with an automatic thermal desorber (ATD, Perkin Elmer, model TurboMatrix 350). The RH was controlled via a humidity controller (Electro-Tech Systems (ETS), Model 514) (I) upstream of the reactor. Concentration of the generated O_3 was measured with an ozone monitor (Model 202, 2B Technologies, An InDevR Company) (K) downstream of the reactor.

The micro reactor, depicted in Fig. 2, was a fixed-bed catalytic reactor containing a coaxial cylindrical quartz tube (ID: 10.4 mm; OD: 12.8 mm; L: 250 mm), with a centered stainless steel-316 rod (D: 5 mm) as an inner electrode. The resulting discharge gap of the reactor was 2.7 mm. Ten (10) centimeter of an aluminum foil was wrapped around the reactor as a ground electrode.

The inner electrode was connected to a high voltage-alternative current power supply (HV-AC) supplier [3]. This HV-AC power supply, illustrated in Fig. 3, constituted a function signal generator (BK PRECISION, Model 4011A) (B), a wideband AC power amplifier (Model AL-600-HF-A, Amp-Line Corp.) (C), and a high voltage transformer box (Model AL-T250-V25/10K-F50/2K, Amp-Line Corp.) (D). This HV-AC provided an adjustable voltage and frequency in the range of 0–30 $kV_{p\text{-}p}$, and 50 Hz to 2 kHz, respectively, to the dielectric barrier discharge (DBD) reactor (F). A digital oscilloscope (Tektronix, TBS1052B-EDU, 50MHZ, 2CHANNEL) (E) monitored the voltage and current signals of the system. A 30 kV high voltage probe (Keysight N2771B) (G) measured the delivered voltage to the reactor. In this study, the frequency was set to 60 Hz and the applied voltage was 16.8 ± 0.1 $kV_{p\text{-}p}$ for isobutanol and 17.6 ± 0.3 $kV_{p\text{-}p}$ for toluene. Selection of the input voltage was based on a series of preliminary tests in order to have the lowest amount of voltage for a stable discharge along with a minimum amount of ozone generation in both dry and humid conditions in the plasma reactor. The applied specific input energy (SIE, $J\,L^{-1}$), as an indicator of energy deposited in the reactor, was calculated as follows:

$$\mathrm{SIE} = \frac{60VI}{Q} \tag{1}$$

In this equation V is the applied voltage (kV); I is the discharge current (mA); Q is the gas flow rate ($L\,min^{-1}$); and 60 is the conversion coefficient [2]. Table 1 specifies the amount of SIE for two level of humidity conditions (RH = 0% and 30%) for toluene and isobutanol.